Multiplicity and Molecular Flexibility in Controlling Molecular Reactivity. Mechanistic and Exploratory Organic Photochemistry[1,2]

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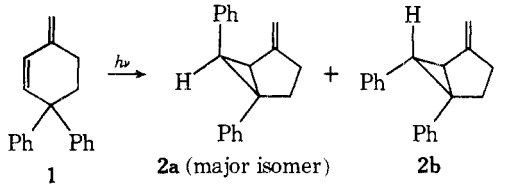
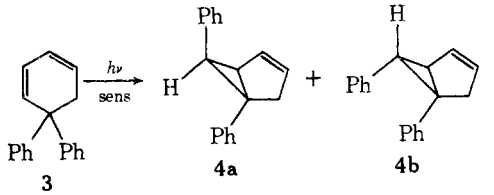
Abstract: The present study was predicated on the observation that 1-methylene-4,4-diphenyl-2-cyclohexene rearranged only when excited to its singlet, while its triplet was unreactive. 2,6,7,7a-Tetrahydro-6,6-diphenylindene and 1,2,6,7,8,8a-hexahydro-2,2-diphenylnaphthalene were selected for study since these have the same chromophore but have the *exo*-methylene moiety incorporated in five- and six-membered rings, respectively. Both the five- and six-ring bicyclic dienes were synthesized and found to undergo photochemical rearrangement with phenyl migration. The structures and stereochemistry of the tricyclic products were elucidated. In contrast to the simple *exo*-methylene monocyclic system, both the single and triplet excited states were found to react. One striking result was the preferential formation of the trans-endo stereoisomer under all conditions. Interestingly, the singlet quantum efficiencies (ϕ = 0.11 and ϕ = 0.12) for the five- and six-ring bicyclic dienes proved not only similar to one another but also close to that of the parent 1-methylene-4,4-diphenyl-2-cyclohexene (ϕ = 0.11). In contrast, the reactivity of the triplets formed a progression. Thus, the parent molecule was already known to be unreactive. The six-ring bicyclic diene had a quantum yield of ϕ = 0.003, while the five-ring bicyclic diene exhibited still further enhanced reactivity (ϕ = 0.36). The results revealed that with increasing flexibility decay processes of the triplet become progressively more efficient. In the case of the singlet, evidence was obtained for an additional decay mechanism, this involving phenyl–diene touching. As a result the overall sensitivity of singlet decay to remote ring flexibility is less than for the triplet.

In our previous investigations we obtained evidence[3] for a common mode of triplet energy dissipation and termed this the free rotor effect. This accounted for the lack of triplet reactivity of 1-methylene-4,4-diphenyl-2-cyclohexene[3a] (**1**) in contrast to the rearrangement of this compound from S_1; note eq 1. Also the free rotor postulate rationalized the general[4,5] lack of reactivity of acyclic di-π-methane systems on sensitization. Strongly supporting this interpretation was the observation that 5,5-diphenyl-1,3-cyclohexadiene (**3**) did rearrange via its triplet;[3b,6] note eq 2. We note that this compound differs from the *exo*-methylene diene **1** primarily by having the second π bond endocyclic and unable to rotate.



(1)

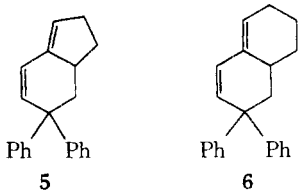
1 **2a** (major isomer) **2b**



(2)

3 **4a** **4b**

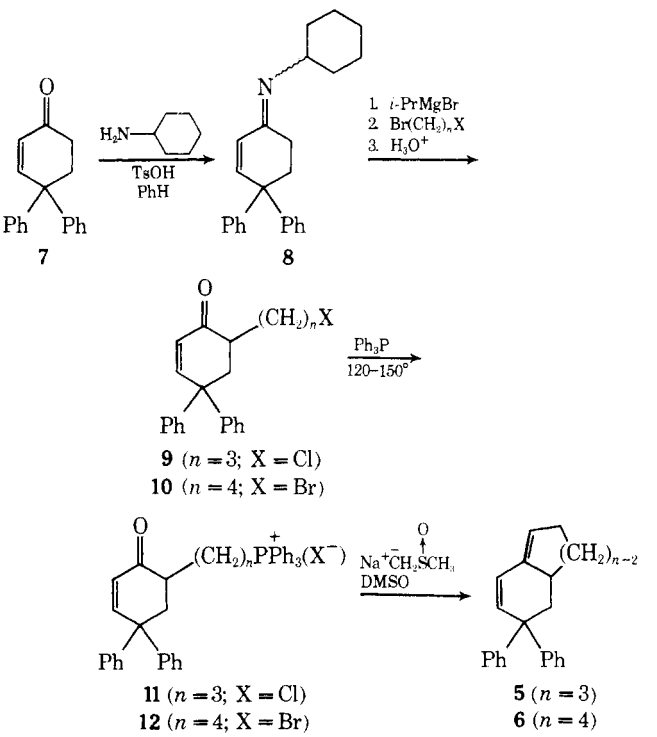
For this study, we selected 2,6,7,7a-tetrahydro-6,6-diphenylindene (**5**) and 1,2,6,7,8,8a-hexahydro-2,2-diphenylnaphthalene (**6**) since these incorporate the diphenyl s-trans diene moiety present in **1** but differ in amount of twisting possible about the distant π bond. Our intention was to compare the reactivity of the two systems with one another and with the parent diphenyldiene **1.**



5 **6**

Results. Synthesis of Reactants. Our approach to the bicyclic dienes **5** and **6** is outlined in Chart I. The readily available 4,4-diphenylcyclohexenone[7] was utilized as a starting material. Alkylation of the enone was accomplished by the method of Stork and Dowd[8] via the iminium conjugate base. However, presently in the case of dihalides, some modification of conditions was necessary, and these are detailed in the Experimental Section.

Chart I. Synthesis of 2,6,7,7a-Tetrahydro-6,6-diphenylindene (**5**) and 1,2,6,7,8,8a-Hexahydro-2,2-diphenylnaphthalene (**6**)



7 **8**

9 (n = 3; X = Cl)
10 (n = 4; X = Br)

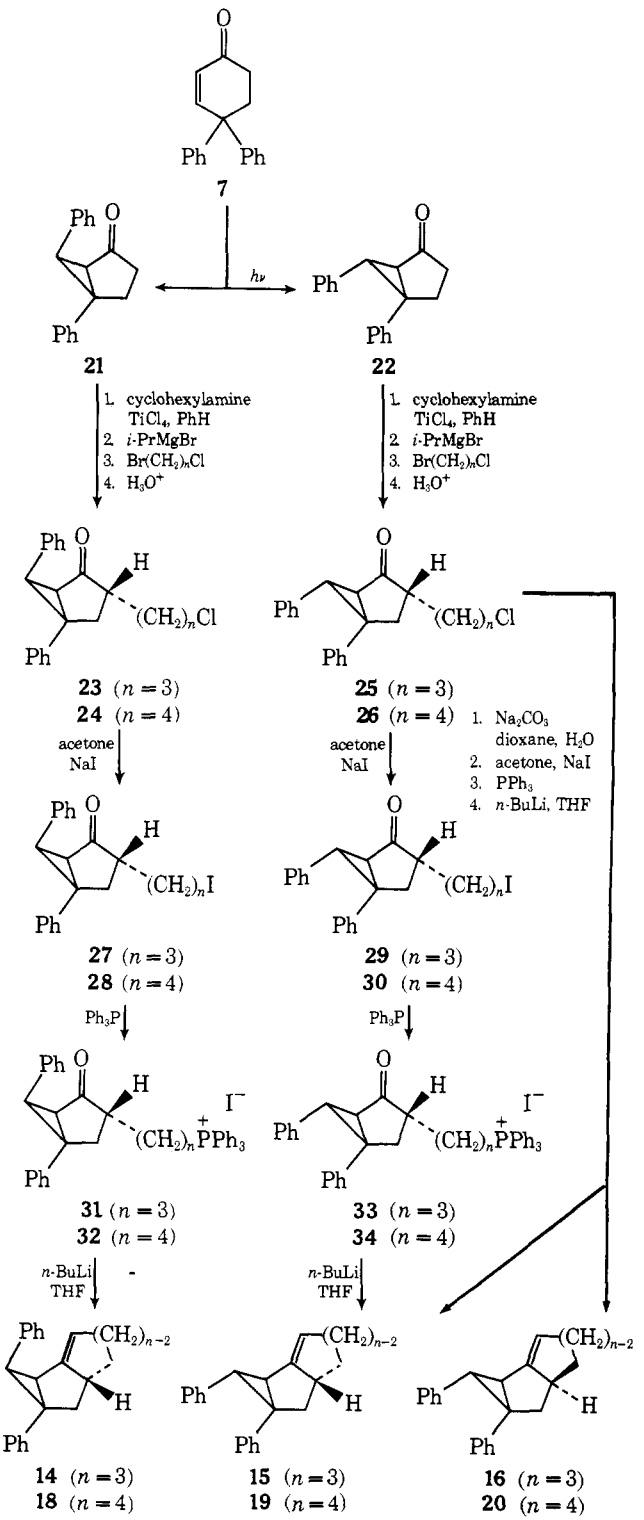
11 (n = 3; X = Cl)
12 (n = 4; X = Br)

5 (n = 3)
6 (n = 4)

Results. Exploratory Photolysis. Our initial efforts were qualitative to determine the reaction course. Thus, in the case of the direct and sensitized irradiations, facile rearrangement was observed using an immersion well apparatus. In both the direct and sensitized irradiations of 2,6,7,7a-tetrahydro-6,6-diphenylindene (**5**), our primary photoproduct predominated, that is, **13,** mp 54–56°. In addition to the main reaction product, a second isomeric product **14,** mp 79.5–81.5°, was formed in considerably lesser amounts. Two other isomeric products were obtained in extremely small amounts; these were **15,** mp 60–62°, and **16,** mp 97–99°.

Similar direct and sensitized irradiations of 1,2,6,7,8,8a-hexahydro-2,2-diphenylnaphthalene (**6**) gave **17,** a colorless oil, as the major photoproduct. In addition, three other isomeric photoproducts were obtained, photoproduct **18,** mp 85–87°, photoproduct **19,** mp 73.7–74.2°, and photoproduct **20,** a colorless oil.

Chart II. Synthesis of *trans*-8,9-Diphenyl-*exo*-tricyclo[6.1.0.0^{2,6}]non-2-ene (**14**), *trans*-8,9-Diphenyl-*exo*-tricyclo[4.4.0.0^{8,10}]dec-1-ene (**18**), *cis*-8,9-Diphenyl-*exo*-tricyclo[6.1.0.0^{2,6}]non-2-ene (**15**), *cis*-8,9-Diphenyl-*endo*-tricyclo[6.1.0.0^{2,6}]non-2-ene (**16**), *cis*-8,9-Diphenyl-*exo*-tricyclo[4.4.0.0^{8,10}]dec-1-ene (**19**), and *cis*-8,9-Diphenyl-*endo*-tricyclo[4.4.0.0^{8,10}]dec-1-ene (**20**)

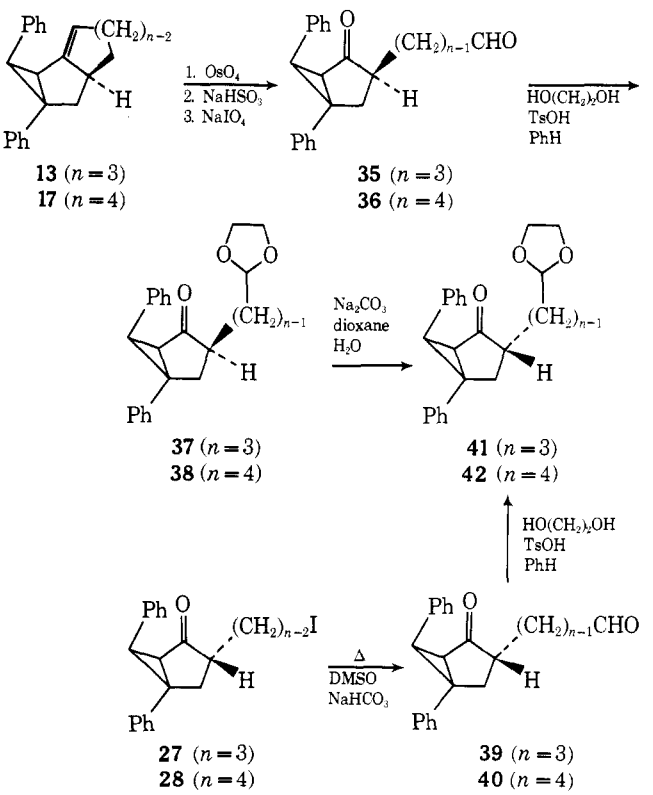


Results. Product Structure Elucidation. The next requirement was determination of the structures of the four photoproducts formed from each of the two bicyclic diene photolyses.

In the case of the five-ring bicyclic diene **5,** the NMR suggested that the reaction had proceeded in a fashion parallel to that of 1-methylene-4,4-diphenyl-2-cyclohexane (**1**) (note eq 1).[3a] Elemental analysis of the major photoproduct **13** revealed it to be an isomer of the starting material **5.** The NMR spectrum revealed a one-hydrogen vinyl multiplet between τ 4.50 and 4.68 coupled with a methylene multiplet at τ 7.48–7.70. Besides the expected ten aromatic hydrogen absorption and a number of complex aliphatic absorptions, a characteristic AB quartet of a *trans*-diphenyl substituted cyclopropane was observed (τ 7.16, 7.48, J = 9 Hz). In an analogous fashion, the six-ring bicyclic diene **6** proceeded to give products that had NMR spectra suggesting diphenyl-substituted vinylcyclopropanes.

Rigorous structural assignments in both the five- and six-ring series derived from synthesis of three of the four respective photoproducts and degradation of the fourth photoproduct to a compound which was then synthesized. These conversions are depicted in Charts II and III.

Chart III. Oxidative Degradation of *trans*-8,9-Diphenyl-*endo*-tricyclo[6.1.0.0^{2,6}]non-2-ene (**13**) and *trans*-8,9-Diphenyl-*endo*-tricyclo[4.4.0.0^{8,10}]dec-1-ene (**17**)



The general synthetic philosophy was the same as for the preparation of the reactant bicyclic dienes **5** and **6.** A preparative photolysis of the known enone **7** gave both *trans*-

Table I. Summary of Direct[a] and Sensitized[b] Quantum Yields for 2,6,7,7a-Tetrahydro-6,6-diphenylindene (5)

Run	Concn of 5,[c] M	Sensitizer, M	% conv	$\phi_{t,endo}$	$\phi_{t,exo}$	$\phi_{c,endo}$	$\phi_{c,exo}$
I-1	0.0028		5	0.108	0.008	0.001	0.002
I-2	0.0029		3	0.103	0.007	0.001	0.002
I-3	0.0030		6	0.091	0.008	0.002	0.004
II-1	0.0029	*m*-Methoxyacetophenone, 0.0120[d]	9	0.209	0.058	0.036	0.063
II-2	0.0054	*m*-Methoxyacetophenone, 0.0104[d]	6	0.227	0.059	0.019	0.048
II-3	0.0054	*m*-Methoxyacetophenone, 0.0103[d]	4	0.248	0.061	0.013	0.036

[a] Black box apparatus employed. [b] Microbench employed. [c] *tert*-Butyl alcohol solvent. [d] 99% of the light absorbed by the sensitizer.

Table II. Summary of Direct and Sensitized Quantum Yields[a] for 1,2,6,7,8,8a-Hexahydro-2,2-diphenylnaphthalene (6)

Run	Concn of 6,[b] M	Sensitizer, M	% conv	$\phi_{t,endo}$	$\phi_{t,exo}$	$\phi_{c,endo}$	$\phi_{c,exo}$
III-1	0.0025		4	0.093	0.029	0.001	0.0004
III-2	0.0023		7	0.096	0.033	0.001	0.0006
III-3	0.0025		9	0.091	0.030	0.001	0.0003
IV-1	0.0017	*m*-Methoxyacetophenone, 0.0029[c]	5	0.0021	0.0010	0.00004	0.00002
IV-2	0.0026	*m*-Methoxyacetophenone, 0.0028[c]	3	0.0021	0.00078	0.00004	0.00001

[a] Black box apparatus. [b] *tert*-Butyl alcohol solvent. [c] >99% of light absorbed by sensitizer.

and *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**21** and **22**) which were readily separated by silica gel chromatography. Formation of the imine of **21** using cyclohexylamine and titanium tetrachloride[9] followed by the Stork–Dowd[8] alkylation (vide supra) with 1-bromo-3-chloropropane or 1-bromo-4-chlorobutane gave *trans*-5,6-diphenyl-*exo*-3-(3-chloropropyl)bicyclo[3.1.0]hexan-2-one (**23**) or *trans*-5,6-diphenyl-*exo*-3-(4-chlorobutyl)bicyclo[3.1.0]hexan-2-one (**24**), respectively. In both systems, only one isomer was formed, and exo stereochemistry at C-3 was assigned. In the alkylation step, the less hindered exo attack is expected.[10] Secondly, this stereochemical assignment is supported by lack of epimerization of the chlorides (**23** and **24**) with base. These observations point strongly to the fact that **23** and **24** have the thermodynamically favored exo configuration. The chloride in **23** and **24** was quantitatively exchanged for iodide to give **27** and **28,** respectively, which gave the phosphonium iodides **31** and **32,** respectively, upon reflux with triphenylphosphine in benzene. The phosphonium salts, **31** and **32,** were smoothly converted under Wittig conditions to the trans,exo tricyclic olefins, **14** and **18,** respectively, whose spectral data matched those of the olefins isolated from the preparative photolysis mixtures of **5** and **6,** respectively. The syntheses of the cis,exo tricyclic olefins **15** and **19** were analogous to the syntheses of **14** and **18** (see Chart II).

However, the cis,endo tricyclic olefins **16** and **20** required an additional step. After the initial alkylation, the chlorides (**25** and **26**) were refluxed with base in an attempt to epimerize at the C-3 position. That proton exchange was taking place was demonstrated by refluxing with deuterium oxide and noting the disappearance of the C-3 proton in the NMR. The mixture, when carried on to the tricyclic olefins, did give a mixture of the cis,endo and cis,exo isomers. When **16** and **20** were separated from **15** and **19,** respectively, their spectral data were identical with the data obtained for the olefins isolated from the preparative photolysis mixtures of **5** and **6,** respectively.

In the case of the major photoproducts **13** and **17,** synthesis proved impractical since exo alkylation is preferred, as shown by the epimerization attempts on **23** and **24.** A degradative structure proof was necessary (see Chart III). *trans*-8,9-Diphenyl-*endo*-tricyclo[6.1.0.$0^{2,6}$]non-2-ene (**13**) and *trans*-8,9-diphenyl-*endo*-tricyclo[4.4.0.$0^{8,10}$]dec-1-ene (**17**) were oxidized with osmium tetroxide to the corresponding glycols which were cleaved with sodium *meta*-periodate to the ketoaldehydes **35** and **36,** respectively, without loss of stereochemistry. These aldehydes were converted to *endo*-acetals **37** and **38,** respectively, which were isomerized with base to the epimeric *exo*-acetals **41** and **42,** respectively. The *exo*-acetals **41** and **42** were obtained from the corresponding *exo*-aldehydes **39** and **40,** respectively, which had been obtained from the Kornblum[11] oxidation of the corresponding iodides **27** and **28,** respectively, shown in Chart III.

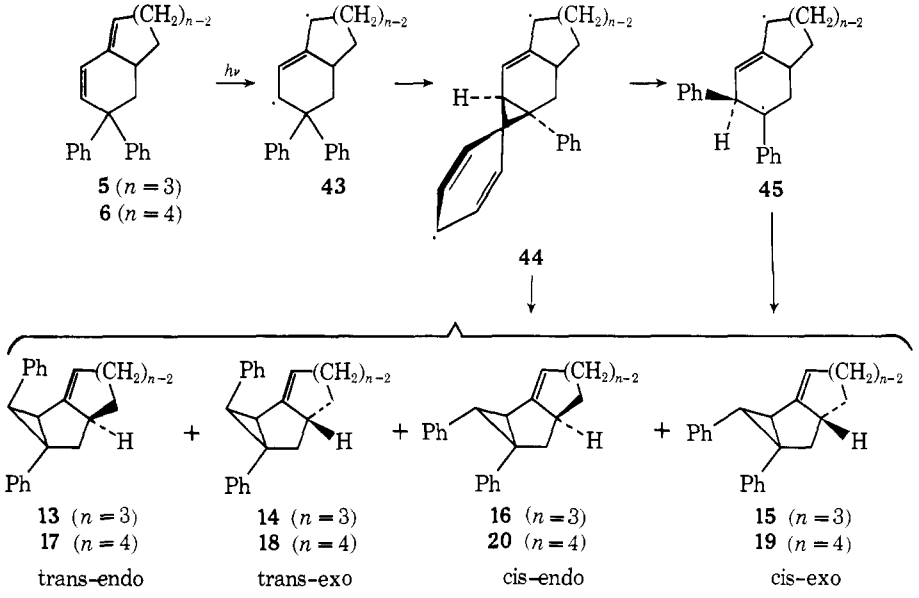
Results. Reaction Efficiencies and Stereoselectivity. The next step was determination of the reaction quantum yields. The black box and microbench apparatus[12] were used. For direct irradiations, 254–304 nm light was used and, for sensitized irradiations, 300–360 nm light was employed. Determinations were run in *tert*-butyl alcohol and were analyzed by gas chromatography. The sensitizer used was *m*-methoxyacetophenone. Low-conversion photolyses were used to minimize absorption of light by photoproducts and to ensure minimal secondary photoreaction. Tables I and II summarize both direct and sensitized quantum yields.

From the quantum efficiency data, we note that the bicyclic dienes (**5** and **6**) are converted overwhelmingly to the trans tricyclic olefins. A more intriguing result is the highly stereoselective predominance of just the trans,endo bicyclic olefin isomers in both direct and sensitized irradiations (see Tables I and II).

Results. The Question of Bicyclobutane Formation. One possible mode of reaction and decay involved bicyclobutane formation of the s-transoid diene moiety.[13] It is known that bicyclobutanes are efficiently trapped by methanol.[13] Thus, control experiments were run both in methanol and with methanol being added at the end of the photolyses. No bicyclobutanes or bicyclobutane adducts were observed. Thus it appears that bicyclobutane formation is not presently involved. The details are described in the Experimental Section.

Results. Singlet Reaction Rates and Decays. The single-photon counting technique in conjunction with systematic reiterative convolution as previously described[14a] permitted determination of the rates of singlet decay and sin-

Chart IV. Resonance Structure Formulation of the Reaction[a]



[a] In excited-state structure **43**, for simplicity, we picture the diene moiety as being excited. While essentially correct for the triplet, in the singlet, excitation is most likely distributed between the two chromophores.

Table III. Summary of the Singlet Lifetimes and Decay Rates of 1-Methylene-4,4-diphenyl-2-cyclohexene (**1**), 2,6,7,7a-Tetrahydro-6,6-diphenylindene (**5**), and 1,2,6,7,8,8a-Hexahydro-2,2-diphenylnaphthalene (**6**)

Compd	Lifetime, nsec	Decay rate (k_{dt}), sec^{-1}	Reaction rate (k_r), sec^{-1}
exo-Methylene diene (**1**)	0.710[a]	1.41×10^9	1.55×10^8
Six-ring bicyclic diene (**6**)	1.24[b]	0.807×10^9	0.970×10^8
Five-ring bicyclic diene (**5**)	2.61[b]	0.383×10^9	0.421×10^8

[a] Emission maximum at 270 nm. [b] Emission maximum at 340 nm.

glet rates of reaction for 1-methylene-4,4-diphenyl-2-cyclohexene (**1**),[14b] 2,6,7,7a-tetrahydro-6,6-diphenylindene (**5**), and 1,2,6,7,8,8a-hexahydro-2,2-diphenylnaphthalene (**6**). The results are summarized in Table III.

Interpretative Discussion. The Reaction. The first observation to be made is that the reaction of both the five- and six-ring bicyclic dienes **5** and **6** proceeds by way of a phenyl migration analogous to that of 1-methylene-4,4-diphenyl-2-cyclohexene (**1**).[3a] This reaction is really a di-π-methane rearrangement[5,15] in which one of the two π moieties is a vinyl group, and the second is the aromatic ring. The reaction may be formulated as in Chart IV.

Interpretative Discussion. Ring Size and Multiplicity Control of Reactivity. The first striking feature of the present results is the finding that the triplet excited states for the two bicyclic dienes, **5** and **6**, do indeed rearrange. This is in dramatic contrast with the case of the triplet of 1-methylene-4,4-diphenyl-2-cyclohexene (**1**) which was found[3a] to be totally unreactive. This provides initial confirmation of the reality of the free rotor effect we postulated earlier since, in the bicyclic diene excited states, free rotation of the exocyclic π bond of the second ring is inhibited.

One can look for reactivity differences deriving from varying size and constraint of the second ring. In addition to this variable, we need to consider the effect of multiplicity on reactivity.

Considering first the effect of ring size in the case of the singlet excited-state reactions, we note the remarkable independence of the reaction quantum yield in proceeding from 1-methylene-4,4-diphenyl-2-cyclohexene (**1**) to the six-ring bicyclic diene **6**, and thence to the five-ring bicyclic diene **5**. These are compared in Table IV.

Table IV. Comparison of Singlet Quantum Yields

Reactant	Reaction quantum yield,[a] ϕ
exo-Methylene diene (**1**)	0.11[b]
Six-ring bicyclic diene (**6**)	0.12
Five-ring bicyclic diene (**5**)	0.11

[a] Refers to the total quantum yield of formation for the photoproducts. [b] Data obtained from ref 3a.

These quantum yields, of course, reflect the ratio of the rates of singlet reaction (i.e., the k_r's) to the total rates of excited singlet decay (i.e., the k_{dt}'s); note eq 3. Single-pho-

$$\phi_r = k_r/k_{dt} \tag{3}$$

ton counting determination[13b] of the lifetimes and the k_{dt}'s led to the results in Table III. Also included in Table III are the k_r's derived from use of eq 3.

Inspection of the k_{dt}'s reveals that the relative constancy of the quantum yields is due to a counterbalancing of these together with the k_r's, giving a constant ratio. Thus there is a decreased rate of decay (i.e., increased lifetime), 710 psec to 1.24 nsec to 2.61 nsec lifetimes, in proceeding from the most flexible *exo*-methylene diene (**1**) to the six-ring bicyclic diene (**6**) to the five-ring bicyclic diene (**5**).

The modest decrease in rate of singlet rearrangement in proceeding from the least strained to the most rigid diene (note Table III) seems most reasonably to derive from the increasing strain encountered as phenyl bridging ensues; note the bridged structure **44** in Chart IV. The parallel rates of singlet decay and reaction suggest that both processes have molecular features in common. For product formation, touching with reaction is a prerequisite, while a major source of decay has been postulated as involving touching-decay. Thus, a molecule touching, or beginning to bridge, can lead onward to product or backward with decay to reactant.

In the case of the triplet, we must consider parallel effects on reactivity. We note a dramatic effect of ring flexibility on the reaction quantum yield (see Table V). This difference could, a priori, arise either from an increased rate of triplet decay with increasing flexibility or from a large increase in triplet reactivity with ring rigidity.[16] Since in the

Table V. Comparison of Triplet Quantum Yields

Reactant	Reaction quantum yield,[a] ϕ
exo-Methylene diene (**1**)	<0.0004[b]
Six-ring bicyclic diene (**6**)	0.003
Five-ring bicyclic diene (**5**)	0.36

[a] Refers to the total quantum yield of formation for the photoproducts. [b] This quantum yield represents the limit of detectability.

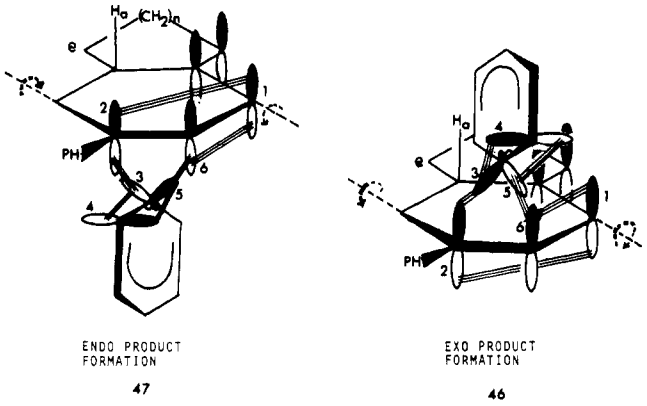


Figure 1. Steric interactions of the migrating phenyl group.

case of the singlet, reactivity (i.e., the k_r's) decreased slightly with rigidity and since there is no obvious reason for the triplet to behave so completely opposite in this regard relative to the singlet, it is concluded that there is indeed a dramatic increase in the rate of triplet decay with ring flexibility.

Thus we are faced with an interesting problem. In the case of singlet excited states, there is a real but very modest increase in excited-state decay with ring flexibility. In the case of the triplets, there is a very large effect of molecular flexibility. Our previous study[2b] on 1-phenylcycloalkene excited singlet and triplet decay mechanisms showed that there are comparable dependences of singlet and triplet decay on free rotation about an excited double bond, although the triplet suffers a slower decay rate by a factor of ca. 10^5 relative to the singlet as a consequence of the multiplicity forbiddenness of decay.

Hence the large dependence of triplet decay on molecular flexibility is expected from our earlier study on the 1-phenylcycloalkenes.[2b] What is unexpected is the lack of parallel singlet decay with increased flexibility. The results strongly suggest that an additional decay mechanism is operative in the singlet and overshadows the free rotor effect in controlling decay.

One very likely candidate for such a decay mechanism is "touching" of the excited phenyl singlet moiety by the diene group of the dienes **1, 5,** and **6.** Intramolecular[17a-d] and intermolecular[17e-j] photophysical processes leading to decay involving contact or near contact between aromatic singlets and alkenes or dienes are well documented.[17] Thus in the present case, singlet decay can have as a major component "touching-decay" which, in effect, is the intramolecular counterpart of intermolecular exciplex formation followed by radiationless decay.[18]

However, another alternative is possible. Thus, the evidence presented (vide supra) shows that emission from the singlets of five-ring and six-ring bicyclic dienes is "diene-like", with a maximum at 340 nm, while emission from *exo*-methylene diene **1** is "phenyl-like", with a maximum at 270 nm.

Further, the literature suggests that the singlet energies of the phenyl and diene moieties may be quite close.[19] Thus, one can envisage two very loosely coupled chromophores of approximately equal singlet excitation energy with emission delicately balanced between the two.

This means that there should be two close-lying singlet excited states, one with excitation heavily localized in the phenyl group and the other with excitation mainly in the diene chromophore. With a free rotor being present in *exo*-methylene diene **1,** one can envisage loss of excitation from the diene moiety more rapidly than equilibration of excitation with the result that emission is from the phenyl chromophore. In contrast, emission from the five- and six-ring diene singlets (**5*** and **6***) derives from the diene portion of the molecule or from both chromophores.

As a consequence, free rotor decay will be less effective in the cases of the five- and six-ring bicyclic dienes since less of the excitation can leak to the flexible, diene chromophore.

This rationale does accommodate the triplet results nicely since here excitation would be expected to be heavily localized in the diene chromophore (E_T = 59 kcal/mol)[23] rather than the phenyl group (E_T = ca. 85 kcal/mol).[20] Excitation localization in the flexible portion of the molecule allow full usage of the free rotor mechanism of decay.

This rationale does not rule out "touching-decay" for the two explanations are not mutually exclusive. Thus, touching may be the mechanism of energy delocalization and leakage to the diene chromophore. In fact, in the second rationale, we are assuming that the rate-limiting step in singlet decay is energy delocalization to the diene, that is "touching".

Interpretative Discussion. Reaction Stereochemistry. Two interesting and general features seem noteworthy in the reaction stereochemistry. One is the preference of *trans*-diphenyl product (*i.e.*, endo) formation. The other is the preference for generation of the *endo*-alkyl ring junction.

In the case of the preference for *trans*-diphenyl stereochemistry, we note that this reaction geometry is ubiquitous in phenyl migrations, not only in hydrocarbon di-π-methane rearrangements[3] but also in enone rearrangements.[26] We have previously made this generalization.[27] The preference is actually for inversion of configuration at the methane carbon (i.e., C-4 of cyclohexenones).

The predominance of the *endo*-alkyl olefins **13** and **17** is an intriguing result which involves the steric interactions of the migrating phenyl group. As seen in Figure 1, when the phenyl migrates from orbital 2 to orbital 6, it encounters severe steric hindrance from the axial hydrogen at the bicyclic ring juncture in structure **46,** but very little steric interaction with the methylene group labeled e. Thus, this is in contrast to the bicyclo[3.1.0] ring systems not having the fused five- and six-membered rings, where the *endo*-alkyl stereoisomer is the less stable one. The ring fusion then flattens out the ring junction making hydrogen a more troublesome than methylene e. Thus there is very little steric interaction encountered in **47.** Thus the preferred products are found to be those in which the migrating phenyl group is anti with respect to the axial hydrogen at the junction. This effect is greatly accentuated in the 2,6,7,7a-tetrahydro-6,6-diphenylindene photochemical rearrangement since the enhanced ring strain increases the steric interactions.

Conclusion

In considering the pattern of reactivity in the di-π-methane rearrangement of diphenyl dienes **1, 5,** and **6,** we see that the singlet reactivity is governed by a modest increase in rearrangement rate as less strain is incurred in phenyl bridging. A fortuitously parallel increase in radiationless decay affords a superficially similar reactivity for the three dienes, in the form of a constant quantum yield. Also, in the

case of singlet reactivity, chromophore touching is seen to overshadow the usual free rotor decay mechanism.

However, for triplets, the chief mode of decay is the free rotor effect, and dramatic differences in reactivity are seen as molecular flexibility is altered.

Thus in organic photochemistry, it is clear that, with more information at one's disposal, one should be able to predict not only facility of rearrangement but also likelihood of decay processes capable of intercepting an excited state before it reacts.

Experimental Section[28]

4,4-Diphenylcyclohexenone. Following the procedure of Zimmerman et al.,[7] 321 g (1.64 mol) of diphenylacetaldehyde and 115 g (1.64 mol) of methyl vinyl ketone in 1920 ml of ether and 29.9 g (0.534 mol) of potassium hydroxide in 180 ml of 95% ethanol yielded 246.6 g (1.00 mol, 61%) of 4,4-diphenylcyclohexenone, mp 95–97° (lit.[7] 91–94°).

***cis*- and *trans*-5,6-Diphenylbicyclo[3.1.0]hexan-2-one.** In a large scale modification of the procedure of Zimmerman and Wilson,[29] a solution of 50.5 g (203 mmol) of 4,4-diphenylcyclohex-2-enone in 5.5 l. of distilled benzene was purged with nitrogen for 2 hr and then irradiated for 47 hr under nitrogen through a 2-mm Pyrex filter with a Hanovia 450-W medium-pressure mercury lamp in a quartz immersion well. The solvent was removed in vacuo to yield a yellow oil which crystallized immediately. The crystals were chromatographed on a 5.5 × 92 cm silica gel column (Matheson Coleman and Bell, grade 62, 60–200 mesh), slurry packed in hexane. Elution in 500-ml fractions gave: fractions 1–4, hexane, nil; 5–8, 1% ether in hexane, nil; 9–12, 2% ether in hexane, nil; 13–16, 3% ether in hexane, 0.1216 g; 17–47, 3% ether in hexane, 43.4 g of *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one; 48–53, 3% ether in hexane, 0.794 g; 54–78, 3% ether in hexane, 5.72 g of *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one. Fractions 17–47 were combined and recrystallized from 95% ethanol to yield 35.7 g (144 mmol, 71%) of *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one, mp 73–74° (lit.[29] 73–74°). Fractions 54–77 were combined and recrystallized from 95% ethanol to yield 4.69 g (18.9 mmol, 9%) of *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one, mp 116–117° (lit.[29] 116.5–117.5°).

4,4-Diphenyl-6-(3-chloropropyl)cyclohex-2-enone. The general method of Stork and Dowd was modified.[8] A mixture of 24.80 g (0.100 mol) of 4,4-diphenylcyclohexenone, 19.8 g (22.8 ml, 0.200 mol) of cyclohexylamine, and 0.07 g of *p*-toluenesulfonic acid in 100 ml of anhydrous benzene was refluxed for ca. 12 hr under a nitrogen atmosphere with azeotropic removal of water. The cooled solution was diluted with an equal volume of benzene and quickly washed with water. The benzene layer was dried and then concentrated in vacuo. Benzene was added and removed in vacuo; the procedure was repeated to remove any residual water. The heavy oil obtained was dissolved in 100 ml of freshly distilled (from lithium aluminum hydride) tetrahydrofuran and added slowly to 0.120 mol of isopropylmagnesium bromide in 100 ml of refluxing tetrahydrofuran over ca. 30 min. The mixture was stirred and refluxed for 3 hr until gas evolution ceased (2.45 l. of propane, 100% of theoretical). The mixture was cooled to 0°, and 31.4 g (21.3 ml, 0.20 mol) of 1-bromo-3-chloropropane was added over 30 sec. The mixture was stirred at 0° for 1 hr and then allowed to warm to room temperature for 20 min. A threefold excess (104 ml) of 10% hydrochloric acid was added slowly, and the mixture was refluxed for ca. 10 hr, then cooled, and two phases were separated. The aqueous phase was extracted with dichloromethane, and the organic extracts were dried and concentrated to yield a reddish brown oil. Hexane was added to the oil and a dark-brown gum separated. The hexane was decanted and filtered, and the gum was washed several times with hexane and ether, then filtered. The filtrate was removed in vacuo to yield 43.0 g of a yellow oil which was chromatographed on a 5 × 70 cm silica gel column (Matheson Coleman and Bell, grade 62, 60–200 mesh), slurry packed in hexane. Elution in 500-ml fractions gave: fractions 1–13, 2% ether in hexane, 5.85 g of 1-bromo-3-chloropropane; 14–28, 2% ether in hexane, 15.69 g of 4,4-diphenyl-6-(3-chloropropyl)cyclohex-2-enone; 29–32, 2% ether in hexane, 1.63 g of a mixture of starting enone and alkylated enone. Fractions 14–28 gave 15.5 g (48 mmol, 48.3%) of 4,4-diphenyl-6-(3-chloropropyl)cyclohex-2-enone, mp 73.5–76.5°, after recrystallization from 95% ethanol.

The spectral data were: ir (CCl_4) 3.26, 3.29, 3.38, 3.40, 3.49, 5.97, 6.26, 6.70, 6.91, 7.24, 7.61, 7.71, 7.83, 8.19, 8.42, 9.42, 9.70, 11.20, 14.35, and 15.35 μ; NMR ($CDCl_3$) τ 2.56–3.05 (m, 11 H, arom and vinyl), 3.90 (d, 1 H, J = 11 Hz, vinyl), 6.60 (t, 2 H, J = 6 Hz, $-CH_2Cl$), 7.0–8.4 (m, 7 H, aliph).

[3-(1-Oxo-4,4-diphenylcyclohex-2-en-6-yl)propyl]triphenylphosphonium Chloride. A mixture of 9.72 g (0.03 mol) of 4,4-diphenyl-6-(3-chloropropyl)cyclohex-2-enone and 7.86 g (0.03 mol) of triphenylphosphine was heated under nitrogen at 140–150° for 18 hr. The resulting brown oil was cooled and precipitated with diethyl ether, filtered and dried in vacuo to yield 17.02 g (29 mmol, 95%) of the white crystalline [3-(1-oxo-4,4-diphenylcyclohex-2-en-6-yl)propyl]triphenylphosphonium chloride, mp 205.5–208.5°.

The spectral data were: ir ($CHCl_3$) 3.00, 3.28, 3.42, 4.08, 5.99, 6.29, 6.72, 6.96, 7.23, 8.20, 9.00, 9.75, 10.04, 11.25, 14.59, and 15.21 μ; NMR ($CDCl_3$) τ 2.00–2.60 (m, 15 H, $P-(C_6H_5)_3$), 2.60–3.00 (m, 11 H, arom and vinyl), 3.96 (d, 1 H, J = 11 Hz, vinyl), 6.00–6.60 (br m, 2 H, $-CH_2P(Ph)_3$), 7.20–8.60 (m, 7 H, aliph).

2,6,7,7a-Tetrahydro-6,6-diphenylindene. Sodium methylsulfinylmethide was prepared by heating and stirring a mixture of 767 mg (32 mmol) of sodium hydride with 50 ml of dimethyl sulfoxide at 70–75° under nitrogen for 1 hr. To the green sodium methylsulfinylmethide solution at room temperature was added dropwise with stirring 17.02 g (29 mmol) of [3-(1-oxo-4,4-diphenylcyclohex-2-en-6-yl)propyl]triphenylphosphonium chloride in 300 ml of dimethyl sulfoxide. The resulting mixture was stirred for 4 hr under nitrogen and poured into 500 ml of water, 470 ml of 10% hydrochloric acid was added, and the resulting mixture was shaken and then extracted with dichloromethane. The combined organic extracts were dried and concentrated in vacuo to yield an orange oil which was added to water and pentane extracted. The combined pentane extracts were dried and concentrated in vacuo. The orange oil produced was chromatographed on a 3 × 110 cm silica gel column (Matheson Coleman and Bell, grade 62, 60–200 mesh), slurry packed in hexane. Elution in 500-ml fractions gave: fractions 1–8, hexane, 7.39 g (27.2 mmol, 92%) of 2,6,7,7a-tetrahydro-6,6-diphenylindene, pure by NMR, which after recrystallization from 95% ethanol had a mp 87.5–89.5°.

The spectral data were: uv λ_{max} (EtOH) 248 (ϵ 27,640), 258 (13,821), sh 270 (1658); ir ($CHCl_3$) 3.27, 3.29, 3.32, 3.38, 3.41, 3.49, 3.51, 6.26, 6.71, 6.92, 7.44, 7.69, 7.79, 8.00, 8.49, 8.68, 8.85, 9.30, 9.52, 9.78, 10.15, 10.54, 11.00, 11.38, 11.69, 12.3, 14.4, and 15.84 μ; NMR ($CDCl_3$) τ 2.76 (s, 5 H, arom), 2.82 (s, 5 H, arom), 3.53 (d, 1 H, J = 10 Hz, vinyl), 3.94 (d, 1 H, J = 10 Hz, vinyl), 4.44 (m, 1 H, vinyl), 7.20–8.20 (m, 6 H, aliph), 8.58 (8 line m, 1 H, cyclopentyl aliph).

***trans*-5,6-Diphenyl-*exo*-3-(3-chloropropyl)bicyclo[3.1.0]hexan-2-one.** The general method of White and Weingarten[9] for enamine preparation together with the Stork procedure[8] for imine alkylation was used. To a stirred solution of 25.0 g (0.101 mol) of *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one and 51.8 ml (0.446 mol) of cyclohexylamine in 300 ml of benzene at 0° under nitrogen was added 8.3 ml (75.4 mmol) of titanium tetrachloride in 10 ml of benzene. The solution was allowed to stir for ca. 18 hr while warming to room temperature, then diluted with ether and water, and vacuum filtered. The organic filtrate layer was washed with water, dried, and concentrated in vacuo to yield 2-cyclohexylimino-*trans*-5,6-diphenylbicyclo[3.1.0]hexane, a yellow oil devoid of a carbonyl absorption in the ir which was used without further purification.

The oil was taken up in 150 ml of freshly distilled (from lithium aluminum hydride) tetrahydrofuran and added dropwise to 119 mmol of isopropylmagnesium bromide in 175 ml of refluxing tetrahydrofuran over ca. 3–4 hr with gas evolution monitoring. The mixture was stirred and refluxed until the gas evolution ceased (2.21 l. of propane, 98% of 2.24 l. theoretical), and 42.8 ml (63.0 g, 0.40 mol) of 1-bromo-3-chloropropane was added over 30 sec to the enamine solution at 0°. The solution was stirred for 20 min and then allowed to come to room temperature over 15 min. An excess (100 ml) of 10% hydrochloric acid was added slowly at room temperature, and the mixture was refluxed with stirring for 1 hr. The reaction mixture was diluted with water and dichloromethane extracted, and the organic extracts were dried and concentrated in vacuo to yield a dark-brown oil. The oil was washed and extracted

with hexane and ether, and the organic filtrate and washings were concentrated in vacuo to give an oil which was chromatographed on a 3.2 × 120 cm silica gel column (Matheson Coleman and Bell, grade 62, 60–200 mesh), slurry packed in hexane. Elution in 500-ml fractions gave: fractions 1–8, hexane, volatile amount of 1-bromo-3-chloropropane; 9–12, 1% ether in hexane, 7.04 g (21.7 mmol, 22%, pure by NMR) of *trans*-5,6-diphenyl-*exo*-3-(3-chloropropyl)bicyclo[3.1.0]hexan-2-one as a colorless oil; 20–27, 10% ether in hexane, 1.70 g of a mixture of the starting ketone and alkylated ketone.

The spectral data were: ir (neat) 3.25, 3.30, 3.40, 3.50, 5.80, 5.95, 6.24, 6.69, 6.91, 7.57, 8.28, 8.49, 9.31, 9.71, 10.35, 10.90, 11.31, 12.30, 13.15, and 14.30 μ; NMR ($CDCl_3$) τ 2.51–2.81 (m, 10 H, arom), 6.72 (t, 2 H, J = 6 Hz, $-CH_2Cl$), 6.91 (d, 1 H, J = 9.5 Hz, benzylic cyclopropyl), 7.32 (d, 1 H, J = 9.5 Hz, α-ketocyclopropyl), 7.40 (d of d, 1 H, J_1 = 12, J_2 = 8 Hz, cyclopentyl), 7.84–8.16 (m, 1 H, α-ketocyclopentyl), 8.16–9.20 (m, 4 H, aliph), 8.40 (d of d, 1 H, J_1 = 12, J_2 = 6 Hz, cyclopentyl); MS *m/e* (%) 326 (2), 325 (3), 296 (7), 288 (15), 248 (2), 220 (10), 219 (30), 207 (40), 206 (10), 205 (50), 191 (16), 189 (10), 178 (9), 141 (10), 129 (14), 128 (16), 115 (16), 98 (17), 91 (100); molecular ion (calcd for $C_{21}H_{21}OCl$, 324.12808) 324.12799.

***trans*-5,6-Diphenyl-*exo*-3-(3-iodopropyl)bicyclo[3.1.0]hexan-2-one.** A mixture of 6.07 g (18.7 mmol) of *trans*-5,6-diphenyl-*exo*-3-(3-chloropropyl)bicyclo[3.1.0]hexan-2-one and 5.61 g (37.4 mmol) of sodium iodide in 100 ml of acetone under nitrogen was refluxed for 24 hr, cooled, concentrated in vacuo, and the resulting solid washed with ether, filtered, and the filtrate concentrated in vacuo to yield 7.70 g (18.7 mmol, >99%) of a dark-brown oil which by NMR was >95% pure iodide. The oil (1.59 g) was chromatographed on a 5 × 30 cm silica gel column (Matheson Coleman and Bell, grade 62, 60–200 mesh), slurry packed in hexane. Elution in 500-ml fractions gave: fractions 1–2, hexane, nil; 3–10, 1% ether in hexane, nil; 11–13, 3% ether in hexane, nil; 14–17, 3% ether in hexane, 1.17 g of *trans*-5,6-diphenyl-*exo*-3-(3-iodopropyl)bicyclo[3.1.0]hexan-2-one as a yellow oil.

The spectral data were: ir (neat) 3.27, 3.30, 3.41, 3.49, 5.81, 5.95, 6.24, 6.32, 6.70, 6.91, 7.59, 8.29, 8.51, 9.29, 9.71, 9.83, 10.00, 10.41, 10.70, 10.90, 11.35, 11.51, 13.11, 13.55, and 14.30 μ; NMR ($CDCl_3$) τ 2.56–2.76 (m, 10 H, arom), 6.86 (d, 1 H, J = 9.5 Hz, benzylic cyclopropyl), 7.04 (t, 2 H, J = 6 Hz, $-CH_2I$), 7.32 (d, 1 H, J = 9.5 Hz, α-ketocyclopropyl), 7.38 (d of d, 1 H, J_1 = 9, J_2 = 14 Hz, cyclopentyl), 7.84–8.20 (m, 1 H, α-ketocyclopentyl), 8.20–9.20 (m, 4 H, aliph), 8.40 (d of d, 1 H, J_1 = 14, J_2 = 8 Hz, cyclopentyl); MS *m/e* (%) 416 (8), 388 (4), 289 (10), 288 (18), 287 (6), 254 (8), 248 (10), 219 (14), 207 (20), 206 (100), 205 (22), 191 (14), 165 (6), 141 (6), 129 (14), 128 (16), 127 (6), 115 (16), 91 (54), 85 (38), 83 (64), and 77 (20); molecular ion (calcd for $C_{21}H_{21}OI$, 416.06363) 416.061064.

[*exo*-3-(*trans*-5,6-Diphenylbicyclo[3.1.0]hex-2-oxo-3-yl)propyl]triphenylphosphonium Iodide. A solution of 7.70 g (18.5 mmol) of *trans*-5,6-diphenyl-*exo*-3-(3-iodopropyl)bicyclo[3.1.0]hexan-2-one and 4.96 g (18.5 mmol) of triphenylphosphine in 100 ml of benzene was refluxed for ca. 3 hr and cooled and the benzene removed in vacuo leaving an oil which was treated with ether to give a solid phosphonium salt which was filtered and washed with ether. The combined ether washings were concentrated in vacuo, 100 ml of benzene was added, and the above 3-hr reflux and work-up detailed above were repeated at least five times giving 5.39 g (7.75 mmol, 42%) of the phosphonium iodide, mp 181–185°

The spectral data were: ir ($CHCl_3$) 2.93, 3.41, 3.49, 4.13, 5.86, 6.24, 6.30, 6.76, 6.97, 7.61, 8.20, 9.00, 9.76, 10.05, 14.55, and 15.18 μ; NMR ($CDCl_3$) τ 2.00–2.40 (m, 15 H, $-P(C_6H_5)_3$), 2.40–3.00 (m, 10 H, arom), 6.20–6.80 (br m, 2 H, $-CH_2-P$), 6.84 (d, 1 H, J = 10 Hz, benzylic cyclopropyl), 7.40 (d, 1 H, J = 10 Hz, α-ketocyclopropyl), 7.40–7.60 (m, 1 H, α-ketocyclopentyl), 7.70–8.00 (m, 1 H, cyclopentyl), 8.00–9.00 (m, 5 H, aliph).

***trans*-8,9-Diphenyl-*exo*-tricyclo[6.1.0.0^{2,6}]non-2-ene.** To a 1.00-g (1.48 mmol) portion of [*exo*-3-(*trans*-5,6-diphenylbicyclo[3.1.0]hex-2-oxo-3-yl)propyl]triphenylphosphonium iodide in 25 ml of freshly distilled tetrahydrofuran (from lithium aluminum hydride) was added dropwise 1.63 mmol (0.856 ml of 1.9 *M*) of *n*-butyllithium dissolved in 25 ml of dry tetrahydrofuran under nitrogen. The resulting mixture was stirred for 3 hr at room temperature, then poured into 250 ml of water, and extracted with dichloromethane. The combined organic extracts were dried and concentrated in vacuo, yielding a pale-yellow residue which was chromatographed on a 2 × 30 cm silica gel column (Matheson Coleman and Bell, grade 62, 60–200 mesh), slurry packed in hexane. Elution in 500-ml fractions gave: fractions 1–2, hexane, 0.220 g (1.10 mmol, 74%) of *trans*-8,9-diphenyl-*exo*-tricyclo[6.1.0.0^{2,6}]non-2-ene, pure by NMR and which had a mp 79.5–81.5° after recrystallization from 95% ethanol.

The spectral data were: uv λ_{max} (EtOH) 220 (28,000), 250 (546), 260 (55); ir (CCl_4) 3.27, 3.30, 3.38, 3.41, 3.50, 6.05, 6.24, 6.71, 6.92, 7.60, 7.81, 8.23, 9.32, 9.48, 9.72, 11.00, 13.80, and 14.34 μ; NMR ($CDCl_3$) τ 2.55–2.88 (m, 10 H, arom), 4.40–4.52 (br m, 1 H, vinyl), 7.24 (d, 1 H, J = 9 Hz, benzylic cyclopropyl), 7.40 (d, 1 H, 9 Hz, allylic cyclopropyl), 7.48–7.80 (m, 3 H, allylic cyclopentyl), 8.00–8.90 (m, 4 H, aliph); MS *m/e* (%) 273 (10), 272 (80), 244 (10), 243 (15), 231 (10), 215 (5), 191 (7), 181 (14), 168 (15), 167 (16), 166 (10), 165 (18), 153 (9), 152 (8), 141 (7), 127 (8), 123 (8), 115 (15), 106 (90), 105 (100), 103 (9), 91 (24), 78 (13), and 77 (100); molecular ion (calcd for $C_{21}H_{20}$, 272.15650) 272.15561.

***cis*-5,6-Diphenyl-*exo*-3-(3-chloropropyl)bicyclo[3.1.0]hexan-2-one.** The general method of White and Weingarten[9] for enamine preparation together with the Stork procedure[8] for imine alkylation was used. To a stirred solution of 11.42 g (46 mmol) of *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one and 23.6 ml (0.204 mol) of cyclohexylamine in 250 ml of benzene at 0° was added 3.79 ml (34.4 mmol) of titanium tetrachloride in ca. 5 ml of benzene. The solution was stirred for ca. 12 hr at room temperature, diluted with ether, then water, and then filtered. The organic layer of the filtrate was water washed, dried, and concentrated in vacuo to yield an imine as a yellow solid which was used without further purification. The imine was taken up in 50 ml of freshly distilled tetrahydrofuran (from lithium aluminum hydride) and added dropwise to 55.2 mmol of isopropylmagnesium bromide in 100 ml of refluxing tetrahydrofuran over a period of 30 min. The mixture was stirred and refluxed for ca. 2 hr until gas evolution ceased (1 l. of propane given off, >99% of theoretical), and 19.6 ml (0.184 mol) of 1-bromo-3-chloropropane was added quickly to the enamine solution at 0°. The solution was stirred at 0° for 1 hr, allowed to come to room temperature over 10 min, and slowly quenched with 46 ml of 10% hydrochloric acid. The mixture was then stirred and refluxed for 1 hr, cooled and, after the addition of water, dichloromethane extracted; the combined organic extracts were dried and concentrated in vacuo to yield a dark-brown oil, which was added to hexane and ether giving a solid by-product, a water soluble salt. The supernatant liquid was decanted and filtered. The combined washings were concentrated in vacuo to give an oil which was chromatographed on a 3 × 100 cm silica gel column (Grace, grade 62, 60–200 mesh), slurry packed in hexane. Elution in 500-ml fractions gave: fractions 1–5, hexane, 4.51 g of 1-bromo-3-chloropropane; 6–9, 1% ether in hexane, nil; 10–11, 1.5% ether in hexane, nil; 12–25, 2% ether in hexane, 8.63 g of *cis*-5,6-diphenyl-*exo*-3-(3-chloropropyl)bicyclo[3.1.0]hexan-2-one; 26–27, 3% ether in hexane, 0.830 g of a mixture of starting ketone and alkylated ketone. Fractions 12–25 were recrystallized from 95% ethanol to yield 5.95 g (18.4 mmol, 40%) of *cis*-5,6-diphenyl-*exo*-3-(3-chloropropyl)bicyclo[3.1.0]hexan-2-one, mp 122–124°.

The spectral data were: ir (CCl_4) 3.27, 3.30, 3.41, 3.49, 5.80, 6.24, 6.70, 6.92, 7.75, 8.25, 8.34, 8.55, 9.35, 9.76, 11.35, and 14.40 μ; NMR ($CDCl_3$) τ 2.60–2.90 (m, 8 H, arom), 2.90–3.20 (m, 2 H, arom), 6.44 (t, 2 H, J = 6.5 Hz, $-CH_2Cl$), 7.00 (d, 1 H, J = 8.0 Hz, benzylic cyclopropyl), 7.12 (d, 1 H, J = 8.0 Hz, α-ketocyclopropyl), 7.16 (d of d, 1 H, J_1 = 3.8, J_2 = 16 Hz, cyclopentyl), 7.30–7.70 (m, 1 H, α-ketocyclopentyl), 7.80–8.80 (m, 4 H, aliph), 8.06 (d of d, 1 H, J_1 = 16, J_2 = 9 Hz, cyclopentyl).

***cis*-5,6-Diphenyl-*exo*-3-(3-iodopropyl)bicyclo[3.1.0]hexan-2-one.** A mixture of 2.02 g (6.23 mmol) of *cis*-5,6-diphenyl-*exo*-3-(3-chloropropyl)bicyclo[3.1.0]hexan-2-one and 1.87 g (12.47 mmol) of sodium iodide in 50 ml of acetone under nitrogen was refluxed for 48 hr and cooled and the acetone removed in vacuo. The resulting solid was washed with ether and filtered and the filtrate concentrated in vacuo to yield 2.30 g (5.55 mmol, 89%) of a yellow solid which by NMR was pure *cis*-5,6-diphenyl-*exo*-3-(3-iodopropyl)bicyclo[3.1.0]hexan-2-one. This was recrystallized from 95% ethanol to give a white solid, mp 119–121°.

The spectral data were: ir (CCl_4) 3.27, 3.30, 3.41, 3.50, 5.80, 6.24, 6.71, 6.92, 8.25, 8.32, 8.56, 8.99, 9.32, 9.76, 11.38, and 14.40

μ; NMR ($CDCl_3$) τ 2.80–3.00 (m, 8 H, arom), 3.00–3.20 (m, 2 H, arom), 6.80 (t, 2 H, J = 6 Hz, $-CH_2I$), 7.02 (d, 1 H, J = 8 Hz, benzylic cyclopropyl), 7.08 (d of d, 1 H, J_1 = 3.5, J_2 = 16 Hz, cyclopentyl), 7.14 (d, 1 H, J = 8 Hz, α-ketocyclopropyl), 7.30–7.70 (m, 1 H, α-ketocyclopentyl), and 7.90–8.70 (m, 4 H, aliph), 8.00 (d of d, 1 H, J_1 = 16, J_2 = 9 Hz, cyclopentyl).

[*exo*-3-(*cis*-5,6-Diphenylbicyclo[3.1.0]hex-2-oxo-3-yl)propyl]triphenylphosphonium Iodide. A solution of 1.75 g (4.21 mmol) of *cis*-5,6-diphenyl-*exo*-3-(3-iodopropyl)dicyclo[3.1.0]hexan-2-one and 1.10 g (4.21 mmol) of triphenylphosphine in 50 ml of benzene was refluxed with stirring for ca. 3 hr and cooled and the benzene removed in vacuo. Ether treatment gave a salt which was filtered and washed with ether. The ether washings were concentrated in vacuo, 50 ml of benzene was added, and the above reflux and work-up was repeated an additional four times giving a total of 1.49 g (2.20 mmol, 52%) of[*exo*-3-(*cis*-5,6-diphenylbicyclo[3.1.0]hex-2-oxo-3-yl)propyl]triphenylphosphonium iodide, mp 92–95°.

The spectral data were: ir ($CHCl_3$) 2.93, 3.41, 3.49, 4.12, 5.86, 6.24, 6.30, 6.75, 6.98, 7.18, 8.20, 9.00, 9.76, 10.05, 11.35, 14.55, and 15.15 μ; NMR ($CDCl_3$) τ 1.90–2.40 (m, 15 H, $P(C_6H_5)_3$), 2.80–3.20 (m, 10 H, arom), 6.00–6.80 (br m, 2 H, CH_2P), 6.90–7.10 (m, 2 H, cyclopropyl), and 7.30–8.40 (m, 7 H, aliph).

***cis*-8,9-Diphenyl-*exo*-tricyclo[6.1.0.0^{2,6}]non-2-ene.** To a stirred suspension of 1.67 g (2.46 mmol) of [*exo*-3-(*cis*-5,6-diphenylbicyclo[3.1.0]hex-2-oxo-3-yl)propyl]triphenylphosphonium iodide in 50 ml of freshly distilled tetrahydrofuran under nitrogen was added dropwise 5.42 mmol of *n*-butyllithium. The solution was stirred at room temperature for 3.5 hr, poured onto 200 ml of ice-water, and extracted with dichloromethane. The organic extracts were combined, dried, and concentrated in vacuo to yield 0.433 g (1.59 mmol, 65%) of a solid which by NMR was pure *cis*-8,9-diphenyl-*exo*-tricyclo[6.1.0.0^{2,6}]non-2-ene. This was recrystallized from 95% ethanol to yield a white solid, mp 60–62°.

The spectral data were: uv λ_{max} (EtOH) 220 (28,932), 250 (2480), 260 (931); ir (CCl_4) 3.26, 3.29, 3.38, 3.41, 3.51, 6.01, 6.24, 6.69, 6.94, 7.79, 8.51, 9.31, 9.76, 10.59, 11.10, and 14.40 μ; NMR ($CDCl_3$) τ 2.70–3.00 (m, 8 H, arom), 3.00–3.20 (m, 2 H, arom), 4.54 (d of d, 1 H, J_1 = 5.5, J_2 = 2.5 Hz, vinyl), 6.84–7.24 (m, 1 H, tertiary allylic cyclopentyl), 7.31 (d, 1 H, J = 7 Hz, benzylic cyclopropyl), 7.40 (d, 1 H, J = 7 Hz, allylic cyclopropyl), 7.47 (d of d, 1 H, J_1 = 12, J_2 = 3 Hz, secondary cyclopentyl), 7.60–7.90 (m, 2 H, allylic cyclopentyl), 8.36 (d of d, 1 H, J_1 = 12, J_2 = 9 Hz, secondary cyclopentyl), 8.40–8.80 (m, 2 H, aliph); MS *m/e* (%) 273 (25), 272 (100), 244 (25), 243 (40), 231 (35), 215 (25), 202 (15), 195 (40), 194 (30), 193 (20), 181 (90), 179 (40), 178 (55), 168 (100), 167 (90), 165 (95), 153 (50), 152 (40), 141 (25), 128 (35), 91 (90), and 77 (35); molecular ion (calcd for $C_{21}H_{20}$, 272.15650) 272.15587.

***cis*-8,9-Diphenyl-*endo*-tricyclo[6.1.0.0^{2,6}]non-2-ene.** A mixture of [*exo*- and *endo*-3-(*cis*-5,6-diphenylbicyclo[3.1.0]hex-2-oxo-3-yl)propyl]triphenylphosphonium iodide was prepared from *cis*-5,6-diphenyl-*exo*-3-(3-chloropropyl)bicyclo[3.1.0]hexan-2-one as described above except that the cis,exo chloride was first refluxed with sodium carbonate, dioxane, and water for 2.5 hr, cooled, dichloromethane extracted, dried, and concentrated in vacuo to give a white solid, mp 122–124°.

Similar treatment with sodium carbonate, dioxane, and deuterium oxide showed by NMR analysis that complete proton exchange at C-3 could be affected. To a stirred suspension of 8.0 g (11.8 mmol) of the equilibrated phosphonium salt in ca. 500 ml of freshly distilled tetrahydrofuran (distilled from lithium aluminum hydride) under nitrogen was quickly added 13.0 mmol of *n*-butyllithium. The solution was stirred for 3.5 hr at room temperature, poured into 50 ml of ice-water, and extracted with dichloromethane. The combined organic extracts were dried and concentrated in vacuo to give an oil which was chromatographed on a 3 × 100 cm silica gel column (Grace, grade 62, 60–200 mesh), slurry packed in hexane. Elution in 500-ml fractions gave: fractions 1–4, hexane, 3.35 g of a mixture of *cis*-8,9-diphenyl-*endo*-tricyclo[6.1.0.0^{2,6}]non-2-ene and *cis*-8,9-diphenyl-*exo*-tricyclo[6.1.0.0^{2,6}]non-2-ene. Fractions 1–4 were combined and rechromatographed on a 100 × 10 cm column of a 3:1 mixture of silicic acid (Mallinkrodt Silic Ar, CC-7, 200–325 mesh) and diatomaceous earth (Eagle Picher Celatom), slurry packed in hexane. Elution in 40-ml fractions and monitored by uv at 256 nm gave: fractions 1–20, hexane, nil; 21–25, hexane, 1.75 g of a mixture of *cis*-8,9-diphenyl-*exo*-tricyclo[6.1.0.0^{2,6}]non-2-ene and *cis*-8,9-diphenyl-*endo*-tricyclo[6.1.0.0^{2,6}]non-2-ene; 26–48, hexane, 1.52 g of a mixture rich in the cis,exo isomer. To separate the two isomers further, high-pressure liquid chromatography was employed. An ALC-100 liquid chromatograph (Waters Associates) was equipped with two 6 ft × $\frac{3}{8}$ in. silicic acid columns (Mallinkrodt Silic AR, CC-7, 200–325 mesh), packed dry and eluted with hexane. Fractions 21–25 (0.102 g) were dissolved in 2 ml of benzene, and 0.5 ml was injected and recycled once. Four injections, each recycled and components collected, yielded 18.9 mg (pure by NMR) of the faster moving (1530 ml retention volume) *cis*-8,9-diphenyl-*endo*-tricyclo[6.1.0.0^{2,6}]non-2-ene, mp 97.0–99.0°, after crystallization from 95% ethanol, and 74.0 mg (pure by NMR) of the slower moving (1890 ml retention volume) *cis*-8,9-diphenyl-*exo*-tricyclo[6.1.0.0^{2,6}]non-2-ene, mp 60–62°, which had ir and NMR spectra identical with those of the independently synthesized material described above.

The spectral data of *cis*-8,9-diphenyl-*endo*-tricyclo[6.1.0.0^{2,6}]non-2-ene were: uv λ_{max} (EtOH) 220 (26,444), 250 (1895), 260 (629); ir (CCl_4) 3.25, 3.29, 3.38, 3.41, 3.51, 6.01, 6.24, 6.69, 6.92, 7.58, 8.51, 9.31, 9.77, 11.05, 11.38, 13.95, and 14.40 μ; NMR ($CDCl_3$) τ 2.90–3.20 (m, 8 H, arom), 3.20–3.32 (m, 2 H, arom), 4.48–4.60 (m, 1 H, vinyl), 6.20–6.70 (br m, 1 H, tertiary allylic cyclopentyl), 7.30–7.40 (m, 1 H, benzylic cyclopropyl), 7.40–7.52 (m, 2 H, allylic cyclopropyl, cyclopentyl), 7.60–7.82 (m, 2 H, aliph), 7.88–8.20 (m, 1 H, allylic cyclopentyl), 8.20–8.90 (m, 2 H, aliph); MS *m/e* (%) 273 (20), 272 (100), 244 (16), 243 (24), 231 (20), 181 (28), 178 (20), 168 (36), 167 (38), 165 (40), 153 (25), 152 (25), 141 (16), 128 (20), 115 (48), 91 (88), and 77 (44); molecular ion (calcd for $C_{21}H_{20}$, 272.15650) 272.15667.

Degradative Oxidation of *trans*-8,9-Diphenyl-*endo*-tricyclo[6.1.0.0^{2,6}]non-2-ene. A solution of 6.82 mg (2.52 mmol) of *trans*-8,9-diphenyl-*endo*-tricyclo[6.1.0.0^{2,6}]non-2-ene and 696 mg (2.77 mmol) of osmium tetroxide in 50 ml of ether was stirred at room temperature under nitrogen for 18 hr. The ether was removed in vacuo to yield a black solid to which were added 5.0 g of sodium bisulfite and 100 ml of 50% ethanol. The solution was stirred and refluxed for 1.5 hr, cooled, filtered, and the black precipitate was washed with ether and ethanol. The filtrate was concentrated in vacuo to yield a clear oil (596 mg, 76%, 1.93 mmol) which was identified as the desired pure glycol (by NMR).

The spectral data were: ir (CCl_4) 2.94, 3.25, 3.29, 3.38, 3.48, 6.25, 6.70, 6.93, 7.80, 7.95, 9.15, 9.29, 9.78, 11.02, and 14.30 μ; NMR ($CDCl_3$) τ 2.40–3.00 (m, 10 H, arom), 5.60 (d of d, 1 H, J_1 = 6, J_2 = 10 Hz, $-CHOH$), 6.20–6.80 (m, 2 H, -OH), 7.08–7.88 (m, 2 H, aliph), 7.32 (d, 1 H, J = 10 Hz, benzylic cyclopropyl), 7.72 (d, 1 H, J = 10 Hz, cyclopropyl), 8.08–9.10 (m, 4 H, aliph), 9.90–10.20 (m, 1 H, aliph); MS *m/e* (%) 306 (20), 288 (8), 272 (8), 270 (8), 261 (16), 207 (20), 206 (100), 205 (26), 202 (12), 191 (18), 192 (8), 193 (9), 178 (10), 165 (14), 167 (10), 141 (10), 129 (18), 128 (20), 115 (28), 91 (70), and 77 (14); molecular ion calcd for $C_{21}H_{22}O_2$; 306.16197, 306.16143.

The glycol (244 mg, 0.80 mmol) and 341 mg (1.68 mmol) of sodium *m*-periodate in 50 ml of 75% ethanol were stirred at room temperature under nitrogen for 3 hr, and 100 ml of water was added. The aqueous mixture was extracted with dichloromethane, and the combined organic extracts were dried and concentrated in vacuo to yield 221 mg (91%) of a brown oil. The above procedure was repeated on a larger scale, and 0.710 g of product was chromatographed on a 20 cm × 10 cm × 2 mm silica gel plate (E. Merck AG Darmstadt, GF-254). After one development with chloroform, the plate was divided into three bands; the bottom band contained 0.589 g of *trans*-5,6-diphenyl-*endo*-3-(3-oxopropyl)bicyclo-[3.1.0]hexan-2-one as a clear oil.

The spectral data were: ir (neat) 2.91, 3.26, 3.29, 3.40, 3.48, 3.66, 5.80, 6.24, 6.68, 6.91, 7.08, 7.19, 7.58, 7.94, 8.30, 8.64, 9.30, 9.70, 10.87, 11.85, 13.11, and 14.30 μ; NMR ($CDCl_3$) τ 0.56 (br s, 1 H, -CHO), 2.60–2.80 (m, 10 H, arom), 6.96 (d, 1 H, J = 10 Hz, benzylic cyclopropyl), 7.24 (d, 1 H, J = 10 Hz, α-ketocyclopropyl), 7.40–8.20 (m, 2 H, aliph), 7.96 (br t, 2 H, J = 8 Hz, CH_2CHO), 8.69–9.16 (m, 2 H, aliph), and 9.22–9.80 (5 br lines, 1 H, side chain aliph); MS *m/e* (%) 305 (20), 304 (80), 248 (14), 247 (28), 232 (15), 231 (16), 207 (24), 206 (100), 205 (50), 191 (30), 141 (7), 129 (24), 128 (30), 115 (28), 103 (14), 91 (100), and 77 (16); molecular ion (calcd for $C_{21}H_{20}O_2$, 304.14632) 304.14642.

Ethylene Acetal of *trans*-5,6-Diphenyl-*endo*-3-(3-oxopropyl)bicyclo[3.1.0]hexan-2-one. A mixture of 0.740 g (2.43 mmol) of *trans*-5,6-diphenyl-*endo*-3-(3-oxopropyl)bicyclo[3.1.0]hexan-2-one, 0.151 g (2.43 mmol) of ethylene glycol, and 10 mg of *p*-toluenesulfonic acid in 50 ml of benzene was refluxed under nitrogen with azeotropic removal of water for 5 hr. The solution was cooled, 50 ml of benzene was added, and the solution was washed with water, saturated sodium bicarbonate solution, and again with water. The benzene layer was dried and concentrated in vacuo to give 0.849 g of a clear oil which was chromatographed on a 3 × 50 cm silica gel column (Grace, grade 62, 60–200 mesh), slurry packed in hexane. Elution in 100-ml fractions gave: 1–3, hexane, nil; 4–7, 5% ether in hexane, 0.637 g (1.69 mmol, 70%) of the desired ethylene acetal of *trans*-5,6-diphenyl-*endo*-3-(3-oxopropyl)bicyclo[3.1.0]hexan-2-one as a clear colorless oil.

The spectral data were: ir (neat) 2.91, 3.26, 3.30, 3.40, 3.48, 5.81, 6.24, 6.69, 6.91, 7.09, 7.56, 7.91, 8.29, 8.76, 9.69, 10.35, 10.59, 11.50, 12.46, 13.10, 13.50, and 14.29 μ; NMR ($CDCl_3$) τ 2.50–2.75 (m, 10 H, arom), 5.42 (t, 1 H, J = 4.5 Hz, O-CH-O), 6.04–6.28 (m, 4 H, $-O-CH_2-$), 6.96 (d, 1 H, J = 10.5 Hz, benzylic cyclopropyl), 7.20 (d, 1 H, J = 10.5 Hz, α-ketocyclopropyl), 7.10–8.40 (m, 2 H, aliph), 7.92 (d of d, 1 H, J_1 = 16, J_2 = 4 Hz, cyclopentyl), 8.40–9.10 (m, 4 H, aliph); MS *m/e* (%) 349 (8), 348 (28), 286 (10), 249 (7), 248 (30), 247 (17), 206 (19), 205 (100), 204 (25), 191 (15), 141 (7), 129 (12), 128 (15), 115 (11), 99 (20), 91 (50), 86 (9), 77 (6), and 73 (35); molecular ion (calcd for $C_{23}H_{24}O_3$, 348.17253) 348.17255.

Oxidation of *trans*-5,6-Diphenyl-*exo*-3-(3-iodopropyl)bicyclo[3.1.0]hexan-2-one. Following a modified Kornblum oxidation[11] procedure, to a stirred suspension of 8.0 g of sodium bicarbonate in 100 ml of dimethyl sulfoxide at 150° under nitrogen was added quickly 2.50 g (6.0 mmol) of *trans*-5,6-diphenyl-*exo*-3-(3-iodopropyl)bicyclo[3.1.0]hexan-2-one in 25 ml of dimethyl sulfoxide. After stirring for 4 min at 150°, the suspension was poured into ice–water and dichloromethane extracted. The combined organic extracts were dried and concentrated in vacuo to yield 1.34 g of a yellow oil which was chromatographed on three 25 cm × 25 cm × 2 mm silica gel plates (E. Merck AG Darmstadt, GF-254). After one development with chloroform, the plates were divided into six bands. The second band from the bottom contained 0.685 g (2.24 mmol, 37%) of *trans*-5,6-diphenyl-*exo*-3-(3-oxopropyl)bicyclo-[3.1.0]hexan-2-one as a colorless oil.

The spectral data were: ir (neat) 3.91, 3.26, 3.30, 3.40, 3.48, 3.66, 5.81, 6.24, 6.70, 6.91, 7.08, 7.20, 7.59, 8.29, 8.49, 8.68, 9.30, 9.70, 10.90, 11.30, 12.21, 13.14, and 14.29 μ; NMR ($CDCl_3$) τ 0.51 (br s, 1 H, -CHO), 2.60–2.84 (m, 10 H, arom), 6.92 (d, 1 H, J = 10 Hz, benzylic cyclopropyl), 7.32 (d, 1 H, J = 10 Hz, α-ketocyclopropyl), 7.42 (d of d, 1 H, J_1 = 8, J_2 = 12 Hz, cyclopentyl), 7.74 (br t, 2 H, J = 7 Hz, CH_2CHO), 7.90–8.40 (m, 2 H, aliph), 8.40–9.20 (m, 2 H, aliph); MS *m/e* (%) 305 (14), 304 (40), 248 (10), 247 (16), 232 (10), 231 (10), 207 (14), 206 (100), 205 (30), 191 (20), 188 (10), 165 (10), 131 (12), 129 (14), 128 (22), 115 (20), 103 (10), 91 (70), and 86 (30); molecular ion (calcd for $C_{21}H_{20}O_2$, 304.14632) 304.14694.

Ethylene Acetal of *trans*-5,6-Diphenyl-*exo*-3-(3-oxopropyl)bicyclo[3.1.0]hexan-2-one. A mixture of 0.740 g (2.43 mmol) of *trans*-5,6-diphenyl-*exo*-3-(3-oxopropyl)bicyclo[3.1.0]hexan-2-one, 0.151 g (2.43 mmol) of ethylene glycol, and 10 mg of *p*-toluenesulfonic acid in 50 ml of benzene was refluxed for 7 hr under nitrogen with azeotropic removal of water. The solution was cooled, diluted with benzene, and washed with water, saturated sodium bicarbonate solution, and again with water. The benzene layer was dried and concentrated in vacuo to give an oil which was chromatographed on a 15 cm × 20 cm × 2 mm silica gel plate (E. Merck AG Darmstadt, GF-254). After one development with 50% ether in hexane, the plate was divided into five bands. The third band from the bottom contained 252 mg (0.72 mmol, 29%) of the desired acetal as a colorless oil. This oil (145 mg) was rechromatographed on a 1.5 × 30 cm silica gel column (Grace, grade 62, 60–200 mesh), slurry packed in hexane. Elution in 125-ml fractions gave: fractions 1–4, 5% ether in hexane, nil; 5–10, 5% ether in hexane, 137 mg of the desired acetal (pure by NMR) that crystallized. Recrystallization from 95% ethanol gave a solid, mp 83–85°.

The spectral data were: ir ($CHCl_3$) 2.91, 3.26, 3.30, 3.40, 3.48, 3.58, 6.24, 6.70, 6.91, 7.10, 7.48, 7.60, 8.88, 9.42, 9.72, 10.61, 11.23, 11.61, 12.14, 13.14, 13.62, and 14.31 μ; NMR ($CDCl_3$) τ 2.54–2.80 (m, 10 H, arom), 5.30 (t, 1 H, J = 4.5 Hz, O-CH-O), 6.10–6.30 (m, 4 H, $-O-CH_2-$), 6.89 (d, 1 H, J = 9.5 Hz, benzylic cyclopropyl), 7.29 (d, 1 H, J = 9.5 Hz, α-ketocyclopropyl), 7.29–7.48 (m, 1 H, α-ketocyclopentyl), 7.80–8.94 (m, 6 H, aliph); MS *m/e* (%) 349 (4), 348 (12), 288 (4), 287 (4), 286 (8), 248 (4), 247 (16), 246 (9), 232 (4), 231 (2), 205 (100), 206 (18), 204 (24), 191 (14), 142 (8), 141 (12), 129 (10), 128 (24), 115 (12), 99 (22), 91 (40), 86 (18), 77 (8), and 73 (30); molecular ion (calcd for $C_{23}H_{24}O_3$, 348.17253) 348.17269.

Epimerization of the Ethylene Acetal of *trans*-5,6-Diphenyl-*endo*-3-(3-oxopropyl)bicyclo[3.1.0]hexan-2-one. A mixture of 90.2 mg (0.259 mmol) of the ethylene acetal of *trans*-5,6-diphenyl-*endo*-3-(3-oxopropyl)bicyclo[3.1.0]hexan-2-one and 100 mg of sodium carbonate in 50 ml of tetrahydrofuran and 10 ml of water were refluxed with stirring for ca. 12 days, and the tetrahydrofuran was removed in vacuo. The resultant oil was diluted with water and extracted with dichloromethane. The combined organic extracts were dried and concentrated in vacuo to give 85 mg (94%) of a yellow oil (>95% pure acetal by NMR) which was crystallized from 95% ethanol to give a white solid, mp 83–85°. This solid had an NMR and ir superimposable with that of the ethylene acetal of authentic *trans*-5,6-diphenyl-*exo*-3-(3-oxopropyl)bicyclo[3.1.0]hexan-2-one derived from the Kornblum oxidation and acetalization. The mixture melting point was not depressed.

Photolysis of 2,6,7,7a-Tetrahydro-6,6-diphenylindene. A solution of 527 mg (1.93 mmol) of 2,6,7,7a-tetrahydro-6,6-diphenylindene in 900 ml of *tert*-butyl alcohol was purged with purified nitrogen[30] for 3 hr and then irradiated for 1.5 hr under purified nitrogen through a 2-mm Corex filter with a Hanovia 450-W medium-pressure mercury lamp in a quartz immersion well. The solvent was removed in vacuo to give a light-yellow oil which was chromatographed initially on a 1.5 × 30 cm silica gel column (Grace, grade 62, 60–200 mesh), slurry packed in hexane. Elution in 500-ml fractions gave: fractions 1–3, hexane, 0.376 g of hydrocarbons (72%); 4–5, hexane, nil; 6–10, ether, 0.1497 (27%) of a yellow oil having broad, uncharacterizable NMR absorptions; total recovery, 99%. Fractions 1–3 were rechromatographed on a 3 × 100 cm column of a 3:1 mixture of silicic acid (Mallinkrodt Silic AR, CC-7, 200–325 mesh) and diatomaceous earth (Eagle Picher Celatom), slurry packed in hexane and monitored by uv. Elution in 40-ml fractions gave: fractions 1–22, hexane, nil; 23–24, hexane, 7.3 mg; 30–34, hexane, 162.8 mg of *trans*-8,9-diphenyl-*endo*-tricyclo[6.1.0.$0^{2,6}$]non-2-ene; 35–40, hexane, 106.2 mg of a mixture of *trans*-8.9-diphenyl-*endo*-tricyclo[6.1.0.$0^{2,6}$]non-2-ene and *trans*-8,9-diphenyl-*exo*-tricyclo[6.1.0.$0^{2,6}$]non-2-ene with a trace of 2,6,7,7a-tetrahydro-6,6-diphenylindene; 41–45, hexane, 28.6 mg of a mixture of *trans*-8,9-diphenyl-*endo*-tricyclo[6.1.0.$0^{2,6}$]non-2-ene, 2,6,7,7a-tetrahydro-6,6-diphenylindene, and *cis*-8,9-diphenyl-*endo*-tricyclo[6.1.0.$0^{2,6}$]non-2-ene; 46–48, hexane, 17.8 mg of a mixture of *cis*-8,9-diphenyl-*endo*-tricyclo[6.1.0.$0^{2,6}$]non-2-ene and *cis*-8,9-diphenyl-*exo*-tricyclo[6.1.0.$0^{2,6}$]non-2-ene.

Separation of the *trans*-8,9-Diphenyl-*endo*-tricyclo[6.1.0.$0^{2,6}$]-non-2-ene and *trans*-8,9-Diphenyl-*exo*-tricyclo[6.1.0.$0^{2,6}$]non-2-ene. High-pressure liquid chromatography was used for preparative separation of the two photoisomers. An ALC-100 liquid chromatograph (Waters Associates) was equipped with a 14 ft × 3/8 in. column (Mallinckrodt Silic AR, CC-7, 200–325 mesh), packed dry and eluted with hexane. In a typical injection 26.5 mg of the isomer mixture was recycled once. The slower moving (1710 ml retention volume) *trans*-8,9-diphenyl-*exo*-tricyclo[6.1.0.$0^{2,6}$]non-2-ene (5.3 mg) could be separated from the faster moving (1440 ml retention volume) *trans*-8,9-diphenyl-*endo*-tricyclo[6.1.0.$0^{2,6}$]non-2-ene (20.1 mg), mp 54–56°, after recrystallization from 95% ethanol.

The spectral data of *trans*-8,9-diphenyl-*endo*-tricyclo[6.1.-0.$0^{2,6}$]non-2-ene were: uv λ_{max} (EtOH) 220 nm (ϵ 15,228), 250 (1015), 260 (508); ir (CCl_4) 3.27, 3.30, 3.38, 3.41, 3.52, 6.05, 6.24, 6.71, 6.92, 7.65, 7.82, 7.98, 8.58, 9.32, 9.48, 9.72, 9.90, 11.00, 12.00, and 14.35 μ; NMR ($CDCl_3$) τ 2.56–3.00 (m, 10 H, arom), 4.50–4.68 (br m, 1 H, vinyl), 6.20–6.69 (br m, 1 H, tertiary allylic cyclopentyl), 7.16 (d, 1 H, J = 9 Hz, benzylic cyclopropyl), 7.48 (d, 1 H, J = 9 Hz, allylic cyclopropyl), 7.48–7.70 (m, 2 H, secondary allylic), 7.86 (d of d, 1 H, J_1 = 14, J_2 = 10 Hz, cyclopentyl), 8.20–8.68 (m, 1 H, aliph), 8.52 (d of d, 1 H, J_1 = 14, J_2 = 10 Hz, cyclopentyl), 9.16–9.64 (eight lines, 1 H, J_1 = 11, J_2 = 11, J_3 = 11, J_4 = 8.5 Hz, aliph); MS *m/e* (%) 273 (10), 272 (80), 244 (10),

243 (15), 231 (10), 215 (5), 191 (7), 181 (14), 168 (15), 167 (16), 166 (10), 165 (18), 153 (9), 152 (8), 141 (7), 127 (8), 123 (8), 115 (15), 106 (90), 105 (100), 103 (9), 91 (24), 178 (13), and 77 (100); molecular ion (calcd for $C_{21}H_{20}$, 272.15650) 272.15561.

The *trans*-8,9-diphenyl-*exo*-tricyclo[6.1.0.0^{2,6}]non-2-ene isomer had ir and NMR spectra identical with those of the independently synthesized material (vide supra).

Separation of the *cis*-8,9-Diphenyl-*endo*-tricyclo[6.1.0.0^{2,6}]non-2-ene and *cis*-8,9-Diphenyl-*exo*-tricyclo[6.1.0.0^{2,6}]non-2-ene Photoproduct Isomers. High-pressure liquid chromatography was used for preparative separation of the two cis photoproducts. The same column and instrument used to separate the trans isomers was used. A mixture from the gravity feed column described above (fractions 46–48, 17.8 mg) in 0.5 ml of benzene was injected and hexane eluted. The slower moving (1485 ml retention volume) *cis*-8,9-diphenyl-*exo*-tricyclo[6.1.0.0^{2,6}]non-2-ene (15.8 mg) could be separated from the faster moving (1260 ml retention volume) *cis*-8,9-diphenyl-*endo*-tricyclo[6.1.0.0^{2,6}]non-2-ene (2.3 mg).

The two isomers had ir and NMR spectra identical with those of the independently synthesized materials (vide supra).

Sensitized Photolysis of 2,6,7,7a-Tetrahydro-6,6-diphenylindene. A solution of 0.536 g (2.00 mmol) of 2,6,7,7a-tetrahydro-6,6-diphenylindene and 0.567 g (3.88 mmol) of *m*-methoxyacetophenone in 750 ml of *tert*-butyl alcohol was purged with purified nitrogen[30] for 2 hr and then irradiated for 2.5 hr through a 2-mm Pyrex filter with a Hanovia 450-W medium-pressure mercury lamp in a quartz immersion well. The solvent was removed in vacuo to yield 1.11 g of a clear oil which was chromatographed on a 3 × 32 cm column (Grace, grade 62, 60–200 mesh), slurry packed in hexane. Elution in 125-ml fractions gave: fractions 1–6, hexane, 0.475 g of starting diene plus tricyclic photoproducts; 6–8, hexane, nil; 9–15, 10% ether in hexane, 0.571 g of *m*-methoxyacetophenone. Fractions 1–6 were rechromatographed on a 2.5 × 170 cm column of a 3:1 mixture of silicic acid (Mallinkrodt Silic AR, CC-7, 200–325 mesh) and diatomaceous earth (Eagle-Picher Celatom), slurry packed in hexane and monitored by uv. Elution in 40-ml fractions gave: 1–21, hexane, nil; 22–26, hexane, 13.1 mg; 27, hexane, 38.5 mg of *trans*-8,9-diphenyl-*endo*-tricyclo[6.1.0.0^{2,6}]non-2-ene; 28–31, hexane, 120.6 mg of a mixture of 2,6,7,7a-tetrahydro-6,6-diphenylindene, *trans*-8,9-diphenyl-*endo*-tricyclo[6.1.0.0^{2,6}]non-2-ene, and *trans*-8,9-diphenyl-*exo*-tricyclo[6.1.0.0^{2,6}]non-2-ene; 32, hexane, 21.7 mg of *trans*-8,9-diphenyl-*exo*-tricyclo[6.1.0.0^{2,6}]non-2-ene and a trace of the trans,endo tricyclic olefin; 33, hexane, 15.1 mg of *cis*-8,9-diphenyl-*endo*-tricyclo[6.1.0.0^{2,6}]non-2-ene; 34–35, hexane, 80.2 mg, cis-endo tricyclic olefin (mp 95–98°), 36–40, hexane, 100.2 mg of a mixture of the cis-endo tricyclic olefin and *cis*-8,9-diphenyl-*exo*-tricyclo[6.1.0.0^{2,6}]non-2-ene; and 41–46, hexane, 80.7 mg of the cis-exo tricyclic olefin (mp 60–63°).

4,4-Diphenyl-6-(4-bromobutyl)cyclohex-2-enone. The general method of Stork and Dowd[8] was modified. A mixture of 12.41 g (0.050 mol) of 4,4-diphenylcyclohexenone, 11.4 ml (9.9 g, 0.100 mol) of cyclohexylamine, and 0.0466 g of *p*-toluenesulfonic acid in 50 ml of benzene was refluxed for ca. 3 hr under nitrogen with azeotropic removal of water. The cooled solution was diluted with benzene and quickly washed with water. The benzene layer was dried and concentrated in vacuo. Benzene was added and removed in vacuo; the procedure was repeated to remove residual cyclohexylamine. The oil obtained was dissolved in 30 ml of dry tetrahydrofuran and added slowly to 0.061 mol of isopropylmagnesium bromide in 50 ml of refluxing tetrahydrofuran over 20 min. The mixture was stirred and refluxed for 2.25 hr and cooled to 0°, and a solution of 24 ml (43.2 g, 0.200 mol) of 1,4-dibromobutane in 25 ml of dry tetrahydrofuran was added over 20 sec. The mixture was then stirred for 30 min while warming to room temperature. A threefold excess (52 ml) of 10% HCl was added slowly; and the mixture was refluxed for 1.3 hr, then cooled, and the two phases were separated. The aqueous phase was extracted with dichloromethane, and the organic extracts were dried and concentrated in vacuo to yield a light-green oil. Hexane was added to the oil and a dark green gum separated. The hexane was decanted and filtered, and the gum was washed several times with hexane and filtered. The hexane was removed in vacuo to yield 47.8 g of a yellow oil which was chromatographed on a 3.5 × 88 cm silica gel column (Matheson Coleman and Bell, grade 62, 60–200 mesh), slurry packed in hexane. Elution in 500-ml fractions gave: fraction 1, hexane, 0.0061 g; 2–5, hexane, 28.20 g, 1,4-dibromobutane; 6–12, 10% methanol in hexane, 0.011 g; 13–17, 10% methanol in hexane, 17.57 g primarily of 4,4-diphenyl-6-(4-bromobutyl)cyclohex-2-enone. Fractions 13–17 were combined and chromatographed on a 3.5 × 87 cm silica gel column, slurry packed in hexane; 500-ml fractions gave: fraction 1, hexane, 0.0077 g; 2–3, 1% ether in hexane, 0.0138 g; 4–13, 1.5% ether in hexane, 0.946 g; 14–27, 1.5% ether in hexane, 12.37 g, 4,4-diphenyl-6-(4-bromobutyl)cyclohex-2-enone; 28–31, 1.5% ether in hexane, 0.859 g of a mixture of starting enone and alkylated enone. Fractions 14–27 were combined to give 12.37 g (0.032 mol, 64%), pure by NMR, of 4,4-diphenyl-6-(4-bromobutyl)cyclohex-2-enone, mp 69–71°, after recrystallization from 95% ethanol.

The spectral data were: NMR ($CDCl_3$) τ 2.76 (m, 11 H, arom and vinyl), 3.89 (d, 1 H, J = 10 Hz, vinyl), 6.68 (t, 2 H, J = 6 Hz, $-CH_2Br$), 7.0–9.0 (m, 9 H, aliph); ir (neat) 3.26, 3.29, 3.40, 3.49, 5.99, 6.29, 6.72, 6.94, 7.25, 8.10, 8.44, 9.00, 9.43, 9.70, 11.20, 12.30, 13.30, and 14.35 μ.

[4-(1-Oxo-4,4-diphenylcyclohex-2-en-6-yl)butyl]triphenylphosphonium Bromide. A mixture of 10.87 g (28.4 mmol) of 4,4-diphenyl-6-(4-bromobutyl)cyclohex-2-enone and 7.44 g (28.4 mmol) of triphenylphosphine was heated at 118–122° for 12 hr under nitrogen. The resulting glass was cooled, pulverized, triturated with 50 ml of acetone, filtered, washed with acetone, and dried in vacuo to yield 15.32 g (23.8 mmol, 84%) of the white crystalline [4-(1-oxo-4,4-diphenylcyclohex-2-en-6-yl)butyl]triphenylphosphonium bromide, mp 197.1–200.0°.

The spectral data were: NMR ($CDCl_3$) τ 2.25 (m, 15 H, arom), 2.76 (m, 11 H, arom and vinyl), 3.94 (d, J = 9.0 Hz, 1 H, vinyl), 6.25 (br m, 2 H, $-CH_2-PPh_3$), 7.0–8.9 (m, 9 H, aliph); ir ($CHCl_3$) 2.45, 3.23, 3.28, 3.37, 3.44, 3.54, 4.05, 5.51, 5.97, 6.28, 6.72, 6.92, 7.21, 7.47, 7.60, 8.16, 8.98, 9.40, 9.71, 10.03, 11.17, 11.65, 12.26, 14.56, and 15.20 μ.

1,2,6,7,8,8a-Hexahydro-2,2-diphenylnaphthalene. Sodium methylsulfinylmethide was prepared by heating and stirring a mixture of 588 mg (24.5 mmol) of sodium hydride with 58 ml of dimethyl sulfoxide at 75° under nitrogen for 45 min. To the sodium methylsulfinylmethide solution at room temperature was added dropwise with stirring 15.15 g (23.5 mmol) of [4-(1-oxo-4,4-diphenylcyclohex-2-en-6-yl)butyl]triphenylphosphonium bromide in 232 ml of dimethyl sulfoxide. The resulting mixture was stirred for 3 hr at room temperature under nitrogen and poured into 520 ml of water. A solution of 520 ml of 10% hydrochloric acid was added, and the resulting mixture was extracted with dichloromethane. The combined organic extracts were dried and concentrated in vacuo. The residue was added to water and pentane extracted, and the combined pentane extracts were dried and concentrated in vacuo to yield a yellow oil and a white solid. The solid and oil were chromatographed on a 3.5 × 88 cm silica gel column (Matheson Coleman and Bell, grade 62, 60–200 mesh), slurry packed in hexane. Elution in 250-ml fractions gave: fractions 1–5, hexane, 0.0297 g; and fractions 6–16, hexane, 5.08 g (17.8 mmol, 75%) of 1,2,6,7,8,8a-hexahydro-2,2-diphenylnaphthalene, a colorless oil.

The spectral data were: uv λ_{max} (EtOH) 230 nm (ϵ 19,900), sh 237 (22,500), 243 (25,400), 260 (4450), sh 270 (920); NMR ($CDCl_3$) τ 2.80 (m, 10 H, arom), 3.77 (d, 1 H, J = 9.6 Hz, vinyl), 4.05 (d, 1 H, J = 10.0 Hz, vinyl), 4.45 (t, 1 H, J = 3.0 Hz, vinyl), 7.4–9.3 (m, 9 H, aliph); ir (neat) 3.21, 3.23, 3.27, 3.38, 3.46, 3.49, 5.14, 5.35, 5.54, 5.77, 6.07, 6.26, 6.69, 6.90, 7.23, 7.48, 7.67, 7.85, 8.12, 8.26, 8.43, 8.66, 8.79, 8.97, 9.17, 9.37, 9.68, 9.96, 10.51, 11.02, 11.49, 11.67, 12.30, 13.30, 13.75, 14.37, 15.49, and 15.93 μ.

***trans*-5,6-Diphenyl-*exo*-3-(4-chlorobutyl)bicyclo[3.1.0]hexan-2-one.** The general method of White and Weingarten[9] for enamine preparation together with the Stork[8] procedure for imine alkylation was used. To a stirred solution of 20.11 g (81.1 mmol) of *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one and 41.7 ml (0.365 mol) of cyclohexylamine in 385 ml of benzene at 0° under nitrogen was added 6.70 ml (60.8 mmol) of titanium tetrachloride in 6.0 ml of benzene. The solution was allowed to stir for 16.5 hr while warming to room temperature and diluted with ether and water, and the solution was vacuum filtered. The organic layer was washed with water, dried, and concentrated in vacuo to yield *trans*-5,6-diphenylbicyclo[3.1.0]hexyl-2-cyclohexylamine, a yellow oil which was used without further purification.

The oil was taken up in 75 ml of freshly distilled tetrahydrofuran and added dropwise to 90.1 mmol of isopropylmagnesium bro-

mide in 65 ml of refluxing tetrahydrofuran over 30 min with gas evolution monitoring. The mixture was stirred and refluxed for 3 hr until the gas evolution ceased (1496 ml of propane, 75% of 1986 ml theoretical), and a solution of 37.5 ml (55.6 g, 0.324 mol) of 1-bromo-4-chlorobutane in 30 ml of dry tetrahydrofuran was added over 30 sec to the enamine solution at 0°. The solution was stirred for 1 hr at 0° and then allowed to warm to room temperature over 15 min. A threefold excess (112 ml) of 10% HCl was added slowly at room temperature, and the mixture was stirred and refluxed for 1.5 hr. The reaction mixture was diluted with water and dichloromethane extracted, and the organic extracts were dried and concentrated in vacuo to yield a red oil. The oil was added to 250 ml of hexane and 100 ml of ether and filtered. The filtrate and washings were concentrated in vacuo to give a red oil which was chromatographed on a 3.5 × 86.5 cm silica gel column (Matheson Coleman and Bell, grade 62, 60–200 mesh), slurry packed in hexane. Elution in 500-ml fractions gave: fractions 1–5, hexane, 27.20 g, 1-bromo-4-chlorobutane; 6–7, 5% ether in hexane, 0.0070 g; 8–14, 10% ether in hexane, 7.709 g, yellow oil containing the desired alkylated product; 15–17, 10% ether in hexane, 0.0357 g. Fractions 8–14 were chromatographed on a 3.5 × 88 cm silica gel column, slurry packed in hexane; 500-ml fractions gave: fractions 1–2, hexane, 0.0050 g; 3–4, 1% ether in hexane, nil; 5–11, 1.5% ether in hexane, 0.0552 g; 12–29, 1.5% ether in hexane, 6.89 g (20.4 mmol, 25%) of *trans*-5,6-diphenyl-*exo*-3-(4-chlorobutyl)bicyclo[3.1.0]hexan-2-one as a pure (by NMR) colorless oil; 30–33, 1.5% ether in hexane, 0.272 g.

The spectral data were: ir ($CHCl_3$) 2.84, 2.93, 3.23, 3.25, 3.29, 3.32, 3.39, 3.49, 5.13, 5.33, 5.54, 5.86 (s), 6.24, 6.34, 6.70, 6.92, 7.08, 7.41, 7.60, 7.64, 7.80, 8.21, 8.53, 9.31, 9.73, 9.85, 10.02, 10.36, 10.69, 11.02, 11.23, 11.60, 12.20, 14.41, 15.46, and 15.81 μ; NMR ($CDCl_3$) τ 2.69 (s, 10 H, arom), 6.61 (t, 2 H, J = 6 Hz, $-CH_2Cl$), 6.90 (d, 1 H, J = 9.4 Hz, benzylic cyclopropyl), 7.35 (d, 2 H, J = 9.4 Hz, α-ketocyclopropyl and cyclopentyl), and 7.69–9.09 (m, 9 H, aliph); MS *m/e* (%) 340 (2), 338 (4), 310 (5), 248 (7), 219 (26), 206 (100), 191 (19), 128 (19), 91 (69), 77 (10); molecular ion (calcd for $C_{22}H_{23}OCl$,[35] 338.14373) 338.14342.

***trans*-5,6-Diphenyl-*exo*-3-(4-iodobutyl)bicyclo[3.1.0]hexan-2-one.** A mixture of 718 mg (2.12 mmol) of *trans*-5,6-diphenyl-*exo*-3-(4-chlorobutyl)bicyclo[3.1.0]hexan-2-one and 637 mg (4.25 mmol) of sodium iodide in 15 ml of acetone under nitrogen was refluxed for 21 hr and cooled, the acetone removed in vacuo, and the resulting solid washed with ether and filtered, and the filtrate concentrated in vacuo to yield a yellow oil. The iodide exchange procedure was repeated to give a 93% yield of *trans*-5,6-diphenyl-*exo*-3-(4-iodobutyl)bicyclo[3.1.0]hexan-2-one, a colorless oil which was pure by NMR.

The spectral data were: ir ($CHCl_3$) 3.26, 3.29, 3.40, 3.48, 5.53, 5.81 (s), 6.26, 6.33, 6.70, 6.92, 7.60, 8.30, 8.56, 8.98, 9.31, 9.53, 9.73, 10.38, 10.98, 11.28, 12.16, 13.14, 13.71, 14.31, 14.73, and 15.86 μ; NMR ($CDCl_3$) τ 2.67 (s, 10 H, arom), 6.88 (d, 1 H, J = 9 Hz, benzylic cyclopropyl), 6.95 (t, 2 H, J = 6 Hz, $-CH_2I$), 7.30 (d, 1 H, J = 9 Hz, α-ketocyclopropyl), 7.37 (m, 1 H, cyclopentyl), and 7.51–9.11 (m, 8 H, aliph); MS *m/e* (%) 430 (3), 402 (2), 303 (1), 248 (5), 219 (9), 206 (100), 191 (9), 127 (3), 91 (21), 77 (4); molecular ion (calcd for $C_{22}H_{23}OI$, 430.079) 430.078.

[*exo*-4-(*trans*-5,6-Diphenylbicyclo[3.1.0]hex-2-oxo-3-yl)butyl]triphenylphosphonium Iodide. A solution of 3.72 g (8.65 mmol) of *trans*-5,6-diphenyl-*exo*-3-(4-iodobutyl)bicyclo[3.1.0]hexan-2-one and 2.55 g (9.75 mmol) of triphenylphosphine in 50 ml of benzene was refluxed for 3.25 hr and cooled, and the benzene was removed in vacuo leaving an oil. The oil was treated with ether to give solid phosphonium salt which was filtered and washed with ether. The combined ether washings were concentrated in vacuo, 40 ml of benzene was added, and the above 3.25-hr reflux and work-up was repeated seven times giving a total of 3.97 g (5.74 mmol, 66%) of the phosphonium iodide, mp 177–180°.

The spectral data were: ir ($CHCl_3$) 2.72, 2.92, 3.27, 3.32, 3.40, 3.48, 4.11, 5.09, 5.29, 5.51, 5.85 (s), 6.24, 6.29, 6.73, 6.96, 7.14, 7.59, 8.15, 8.22, 8.28, 8.49, 8.99, 9.29, 9.72, 9.84, 10.02, 10.25, 10.68, 10.91, 11.28, 11.67, 12.18, 12.31, 14.52, 15.19, and 15.84 μ; NMR ($CDCl_3$) τ 1.96–2.45 (m, 15 H, $-P(C_6H_5)$), 2.52–2.97 (m, 10 *H*, arom), 6.12–6.73 (broad t, 2 H, J = 7 Hz, $-CH_2-P$), 6.91 (d, 1 H, J = 9 Hz, benzylic cyclopropyl), 7.39 (d, 1 H, J = 9 Hz, α-ketocyclopropyl), 7.48 (m, 1 H, cyclopentyl), 7.57–9.17 (m, 8 H, aliph).

***trans*-8,9-Diphenyl-*exo*-tricyclo[4.4.0.0^{8,10}]dec-1-ene.** To a stirred suspension of 584 mg (0.845 mmol) of [*exo*-4-(*trans*-5,6-diphenylbicyclo[3.1.0]hex-2-oxo-3-yl)butyl]triphenylphosphonium iodide in 15 ml of freshly distilled tetrahydrofuran under nitrogen was added 1.55 mmol of *n*-butyllithium in 15 ml of tetrahydrofuran. The solution was stirred at room temperature for 5 hr, poured into ice-water, and dichloromethane extracted. The organic extracts were dried and concentrated in vacuo to yield 525 mg of a yellow oil which was chromatographed on a 1.8 × 25.5 cm silica gel column (Grace, grade 62, 60–200 mesh), slurry packed in hexane. The first 250 ml of hexane afforded 198 mg of solid. Recrystallization from 95% ethanol gave 184 mg (0.642 mmol, 76%) of *trans*-8,9-diphenyl-*exo*-tricyclo[4.4.0.0^{8,10}]dec-1-ene, mp 85–87°.

The spectral data were: ir ($CDCl_3$) 3.24, 3.27, 3.31, 3.42, 3.50, 3.53, 3.78, 4.47, 5.14, 5.36, 5.56, 5.99, 6.24, 6.35, 6.70, 6.92, 7.11, 7.48, 7.52, 7.58, 7.69, 7.80, 7.99, 8.12, 8.25, 8.39, 8.72, 8.78, 9.33, 9.45, 9.51, 9.72, 9.87, 10.02, 10.25, 10.62, 11.21, 12.30, 12.45, 14.50, 15.00, and 15.68 μ; NMR ($CDCl_3$) τ 2.52–2.92 (m, 10 H, arom), 4.52 (broad t, 1 H, J = 2 Hz, vinyl), 7.36 (d, 1 H, J = 9.2 Hz, benzylic cyclopropyl), 7.45 (d, 1 H, J = 9.2 Hz, allylic cyclopropyl), 7.67 (d of d, 1 H, J_1 = 6, and J_2 = 7 Hz, allylic cyclopentyl), 7.85–8.51 (m, 5 H, aliph), and 8.61–9.35 (m, 3 H, aliph); uv λ_{max} (EtOH) 202 nm (ϵ 31,200), sh 217 (16,250), 255 (2090), 270 (180).

***cis*-5,6-Diphenyl-*exo*-3-(4-chlorobutyl)bicyclo[3.1.0]hexan-2-one.** The general method of White and Weingarten[9] for enamine preparation together with the Stork[8] procedure for imine alkylation was used. To a stirred solution of 4.06 g (16.4 mmol) of *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one and 8.44 ml (7.31 g, 73.8 mmol) of cyclohexylamine in 75 ml of benzene at 0° was added 1.35 ml (2.33 g, 12.3 mmol) of titanium tetrachloride in 1.0 ml of benzene. The solution was stirred for 18 hr at room temperature, diluted with ether, then water, and filtered. The organic layer of the filtrate was water washed, dried, and concentrated in vacuo to yield imine as a tan solid which was used without purification. This was taken up in 15 ml of freshly distilled tetrahydrofuran and added dropwise over 10 min to 19.5 mmol of isopropylmagnesium bromide in 15 ml of refluxing tetrahydrofuran. The mixture was stirred and refluxed for 3.5 hr until gas evolution ceased (326 ml of propane given off, 81% of theoretical, 401 ml), and a solution of 7.57 ml (11.3 g, 65.6 mmol) of 1-bromo-4-chlorobutane in 7.0 ml of tetrahydrofuran was added quickly to the enamine solution at 0°. The solution was stirred at 0° for 1 hr, allowed to come to room temperature over 15 min, and a threefold excess (23 ml) of 10% hydrochloric acid was added slowly. The mixture was stirred and refluxed for 1.75 hr and cooled, water was added, and the mixture was dichloromethane extracted. The combined organic extracts were dried and concentrated in vacuo to yield a red oil, which was added to hexane and ether giving a solid by-product. The supernatant liquid was decanted and filtered. The combined washings were concentrated in vacuo to give a red oil which was chromatographed on a 3.5 × 86 cm silica gel column (Grace, grade 62, 60–200 mesh), slurry packed in hexane. Elution in 500-ml fractions gave: fractions 1–4, hexane, 5.57 g, 1-bromo-4-chlorobutane; 5–6, 1% ether in hexane, nil; 7–17, 3% ether in hexane, nil; 18–22, 3% ether in hexane, 2.36 g of *cis*-5,6-diphenyl-*exo*-3-(4-chlorobutyl)bicyclo[3.1.0]hexan-2-one; 23–25, 3% ether in hexane, 0.196 g, mixture of starting ketone and alkylated ketone; 26–29, 3% ether in hexane, 1.30 g, starting ketone; and 30–32, 3% ether in hexane, 0.0165 g. Fractions 18–22 were recrystallized from 95% ethanol to yield 2.14 g (6.31 mmol, 38%) of *cis*-5,6-diphenyl-*exo*-3-(4-chlorobutyl)bicyclo[3.1.0]hexan-2-one, mp 105.1–107.1°.

The spectral data were: ir ($CHCl_3$) 3.33, 3.42, 3.50, 5.84 (s), 6.24, 6.71, 6.92, 7.22, 7.42, 7.66, 7.82, 8.14, 8.26, 8.35, 8.53, 8.83, 9.32, 9.77, 10.42, 11.01, 11.32, 14.42, 15.02, and 15.42 μ; NMR ($CDCl_3$) τ 2.75–3.32 (m, 10 H, arom), 6.53 (t, 2 H, J = 6.5 Hz, $-CH_2Cl$), 7.08 (d, 1 H, J = 8 Hz, benzylic cyclopropyl), 7.20 (d, 1 H, J = 8 Hz, α-ketocyclopropyl), 7.24 (d of d, 1 H, J_1 = 15, J_2 = 4 Hz, cyclopentyl), 7.44–7.80 (m, 1 H, α-ketocyclopentyl), and 7.88–8.98 (m, 7 H, aliph).

***cis*-5,6-Diphenyl-*exo*-3-(4-iodobutyl)bicyclo[3.1.0]hexan-2-one.** A mixture of 1.00 g (2.97 mmol) of *cis*-5,6-diphenyl-*exo*-3-(4-chlorobutyl)bicyclo[3.1.0]hexan-2-one and 922 mg (6.16 mmol) of sodium iodide in 18 ml of acetone under nitrogen was refluxed for 18 hr and cooled, the acetone was removed in vacuo, and the resulting solid was washed with ether, filtered, and the filtrate was

concentrated in vacuo to yield a white solid. This material was subjected to the same procedure to complete the iodide exchange, thus giving 1.22 g of a white solid which was recrystallized from 95% ethanol to yield 1.14 g (2.65 mmol, 89%) of *cis*-5,6-diphenyl-*exo*-3-(4-iodobutyl)bicyclo[3.1.0]hexan-2-one, mp 126–127°.

The spectral data were: ir ($CHCl_3$) 2.88, 3.30, 3.33, 3.40, 3.49, 5.83 (s), 6.24, 6.70, 6.92, 7.00, 7.19, 7.40, 7.53, 7.73, 8.15, 8.34, 8.53, 8.94, 9.31, 9.75, 10.50, 10.65, 11.04, 11.20, 11.29, 12.80, 14.40, and 15.07 μ; NMR ($CDCl_3$) τ 2.74–3.38 (m, 10 H, arom), 6.87 (t, 2 H, J = 7 Hz, $-CH_2I$), 7.23 (d of d, 1 H, J_1 = 4, J_2 = 16 Hz, cyclopentyl), 7.08 (d, 1 H, J = 8.0 Hz, benzylic cyclopropyl), 7.20 (d, 1 H, J = 8.0 Hz, α-ketocyclopropyl), 7.45–7.80 (m, 1 H, α-ketocyclopentyl), and 7.92–8.97 (m, 7 H, aliph).

[*exo*-4-(*cis*-5,6-Diphenylbicyclo[3.1.0]hex-2-oxo-3-yl)butyl]triphenylphosphonium Iodide. A solution of 803 mg (1.87 mmol) of *cis*-5,6-diphenyl-*exo*-3-(4-iodobutyl)bicyclo[3.1.0]hexan-2-one and 671 mg (2.56 mmol) of triphenylphosphine in 15 ml of benzene was refluxed with stirring for 5 hr and cooled, and the benzene was removed in vacuo. Ether treatment gave phosphonium salt which was filtered and washed with ether. The ether washings were concentrated in vacuo, 12 ml of benzene was added, and the above reflux and work-up was repeated four times giving a total of 819 mg (1.18 mmol, 63%) of [*exo*-4-(*cis*-5,6-diphenylbicyclo[3.1.0]hex-2-oxo-3-yl)butyl]triphenylphosphonium iodide, mp 98–102°.

The spectral data were: ir ($CHCl_3$) 2.95, 3.28, 3.30, 3.34, 3.41 (s), 3.49, 4.11, 5.29, 5.56, 5.83 (s), 6.23, 6.30, 6.73, 6.96, 7.14, 7.16, 7.21, 7.51, 7.61, 7.64, 8.15, 8.23, 8.30, 8.52, 9.00 (s), 9.31, 9.53, 9.77, 10.03, 10.66, 11.01, 11.17, 11.31, 14.48, 14.56 (s), 14.62, and 15.19 μ; NMR ($CDCl_3$) τ 1.92–2.70 (m, 15 H, $-P(C_6H_5)$), 2.76–3.32 (m, 10 H, arom), 6.36 (broad m, 2 H, $-CH_2-P$), 6.98 (d, 1 H, J = 6.0 Hz, benzylic cyclopropyl), 7.06 (d, 1 H, J = 6.0 Hz, α-ketocyclopropyl), 7.28–7.72 (m, 3 H, aliph), and 7.92–8.92 (m, 6 H, aliph).

***cis*-8,9-Diphenyl-*exo*-tricyclo[4.4.0.0^{8,10}]dec-1-ene.** To a stirred suspension of 614 mg (0.887 mmol) of [*exo*-4-(*cis*-5,6-diphenylbicyclo[3.1.0]hex-2-oxo-3-yl)butyl]triphenylphosphonium iodide in 20 ml of freshly distilled tetrahydrofuran under nitrogen was added dropwise 1.5 mmol of *n*-butyllithium, and the solution was stirred at room temperature under nitrogen for 3 hr. The mixture was then poured into 200 ml of ice–water and extracted with dichloromethane. The organic extracts were combined, dried, and concentrated in vacuo to yield 540 mg of a yellow oil which was chromatographed on a 1.8 × 30 cm silica gel column (Grace, grade 62, 60–200 mesh), slurry packed in hexane. The first 250 ml of hexane afforded 160 mg of a white solid. Recrystallization from 95% ethanol gave 150 mg (0.524 mmol, 59%) of *cis*-8,9-diphenyl-*exo*-tricyclo[4.4.0.0^{8,10}]dec-1-ene, mp 73.7–74.2°.

The spectral data were: ir ($CHCl_3$) 3.23, 3.26, 3.30, 3.40, 3.48, 3.50, 3.76, 5.14, 5.36, 5.56, 5.77, 5.98, 6.23, 6.33, 6.68, 6.91, 7.21, 7.42, 7.50, 7.80, 7.89, 8.30, 8.73, 8.80, 9.21, 9.33, 9.73, 10.28, 10.63, 11.03, 11.22, 11.35, 11.46, 11.69, 13.70, 14.33, and 15.08 μ; NMR ($CDCl_3$) τ 2.59–3.62 (m, 10 H, arom), 4.39 (d of d, 1 H, J_1 = 7, J_2 = 3.2 Hz, vinyl), 7.28–7.54 (m, 1 H, tertiary allylic), 7.36 (d, 1 H, J = 8 Hz, benzylic cyclopropyl), 7.46 (d, 1 H, J = 8 Hz, allylic cyclopropyl), and 7.56–9.26 (m, 8 H, aliph); uv λ_{max} (EtOH) 209 nm (ϵ 18,490), sh 220 (16,210), sh 265 (705), sh 275 (343).

***cis*-8,9-Diphenyl-*endo*-tricyclo[4.4.0.0^{8,10}]dec-1-ene.** A mixture of [*exo*- and *endo*-4-(*cis*-5,6-diphenylbicyclo[3.1.0]hex-2-oxo-3-yl)butyl]triphenylphosphonium iodide was prepared as described above from *cis*-5,6-diphenyl-3-*exo*-4-chlorobutyl)bicyclo-[3.1.0]hexan-2-one except that the cis–exo chloride was first refluxed with anhydrous sodium carbonate, dioxane, and water for 3.5 hr, cooled, dichloromethane extracted, dried, and concentrated in vacuo to give a white solid, mp 103–106°. Similar treatment with anhydrous sodium carbonate, dioxane, and deuterium oxide showed by NMR analysis that complete proton exchange at C-3 could be effected. To a stirred suspension of 698 mg (1.01 mmol) of the phosphonium salt in 25 ml of tetrahydrofuran under nitrogen was quickly added 2.02 mmol of *n*-butyllithium. The solution was stirred for 2.5 hr at room temperature, poured over 200 ml of ice–water, and extracted with dichloromethane. The combined organic extracts were dried and concentrated in vacuo to give a yellow oil which was chromatographed on a 2 × 29 cm silica gel column, slurry packed in hexane. Elution in 125-ml fractions gave: fractions 1–3, hexane, nil; 4–9, 86 mg of a mixture of *cis*-8,9-diphenyl-*endo*-tricyclo[4.4.0.0^{8,10}]dec-1-ene and *cis*-8,9-diphenyl-*exo*-tricyclo[4.4.0.0^{8,10}]dec-1-ene. Fractions 4–9 were combined and rechromatographed on a 2.5 × 139 cm column of a 3:1 mixture of silicic acid (Mallinkrodt Silic AR, CC-7, 200–325 mesh) and diatomaceous earth (Eagle-Picher Celatom), slurry packed in hexane. Elution in 40-ml fractions gave: fractions 1–35, hexane, nil; 36–37, 25 mg of *cis*-8,9-diphenyl-*endo*-tricyclo[4.4.0.-0^{8,10}]dec-1-ene (0.087 mmol, 8%); 38–43, 45 mg of *cis*-8,9-diphenyl-*exo*-tricyclo[4.4.0.0^{8,10}]dec-1-ene; and 44–50, 7 mg.

The spectral data were: NMR ($CDCl_3$) τ 2.58–3.32 (m, 10 H, arom), 4.30–4.50 (br m, 1 H, vinyl), 6.80–7.30 (m, 1 H, tertiary allylic), 7.23–7.29 (m, 2 H, cyclopropyl), 7.40–9.20 (m, 8 H, aliph); ir ($CHCl_3$) 3.28, 3.30, 3.41, 3.50, 6.24, 6.70, 6.92, 7.53, 8.40, 8.70, 9.32, 9.72, 11.04, 11.75, 12.65, 13.20, and 14.36 μ; uv λ_{max} (EtOH) 210 nm (ϵ 18,430), sh 222 (16,150), sh 265 (705), sh 275 (352). This procedure proved capricious and often led almost totally to cis–exo diene.

Degradative Oxidation of *trans*-8,9-Diphenyl-*endo*-tricyclo[4.4.0.0^{8,10}]dec-1-ene. A solution of 275 mg (0.961 mmol) of *trans*-8,9-diphenyl-*endo*-tricyclo[4.4.0.0^{8,10}]dec-1-ene and 346 mg (1.36 mmol) of osmium tetroxide in 40 ml of ether was stirred at room temperature under nitrogen for 18 hr. The ether was removed in vacuo to yield a black solid to which was added 1.99 g (19.1 mmol) of sodium bisulfite and 50 ml of 50% ethanol. The solution was stirred and refluxed for 1.75 hr, cooled, and filtered, and the precipitate washed with ether and ethanol. The filtrate was concentrated in vacuo to give a white solid which was taken up in dichloromethane, washed with water, dried, and concentrated in vacuo to yield a brown oil (307 mg) which ir and NMR showed to be the desired glycol. Further purification of the glycol was not attempted.

The crude glycol (200 mg) and 271 mg (1.27 mmol) of sodium *m*-periodate in 40 ml of 75% ethanol were stirred at room temperature under nitrogen for 3.5 hr, and 100 ml of water was added. The aqueous mixture was extracted with dichloromethane, and the combined organic extracts were dried and concentrated in vacuo to yield 160 mg of a brown oil which was chromatographed on a 20 cm × 10 cm × 2 mm silica gel plate (E. Merck AG Darmstadt, GF-254). After one development with chloroform, the plate was divided into four bands; the second band from the bottom contained 67 mg (0.21 mmol, 34%) of *trans*-5,6-diphenyl-*endo*-3-(4-oxobutyl)bicyclo[3.1.0]hexan-2-one (pure by NMR).

The spectral data were: NMR ($CDCl_3$) τ 0.45 (t, 1 H, J = 1.3 Hz, CHO), 2.50–2.85 (m, 10 H, arom), 6.94 (d, 1 H, J = 10 Hz, benzylic cyclopropyl), 7.21 (d, 1 H, J = 10 Hz, α-ketocyclopropyl), 7.24–7.48 (m, 1 H, α-ketocyclopentyl), 7.48–7.76 (m, 2 H, $-CH_2CHO$), 7.76–8.04 (m, 3 H, cyclopentyl and aliph side chain), and 8.52–9.24 (m, 3 H, cyclopentyl and aliph side chain); ir ($CHCl_3$) 2.88, 3.33, 3.40, 3.49, 3.68, 5.84 (s), 6.24, 6.70, 6.91, 7.21, 7.59, 7.91, 8.21, 8.76, 9.31, 9.72, 10.10, 11.03, and 14.40 μ; MS *m/e* (%) 318 (31), 300 (5), 290 (3), 248 (2), 231 (7), 219 (6), 206 (100), 191 (19), 128 (13), 91 (56), 77 (8).

Ethylene Acetal of *trans*-5,6-Diphenyl-*endo*-3-(4-oxobutyl)bicyclo[3.1.0]hexan-2-one. A mixture of 91 mg (0.29 mmol) of *trans*-5,6-diphenyl-*endo*-3-(4-oxobutyl)bicyclo[3.1.0]hexan-2-one, 0.30 mmol (17 μl.) of ethylene glycol, and 2 mg of *p*-toluenesulfonic acid in 5 ml of benzene was refluxed under nitrogen with azeotropic removal of water for 7 hr. The solution was cooled, 10 ml of benzene was added, and the solution was washed with water, saturated sodium bicarbonate solution, and water again. The benzene layer was dried and concentrated in vacuo to give 91 mg of a dark oil which was chromatographed on a 5 cm × 20 cm × 2 mm silica gel plate (E. Merck AG Darmstadt, GF-254). After two developments with 50% ether in hexane, the plate was divided into three bands. The middle band contained 15 mg of the desired acetal as a colorless oil.

The spectral data were: NMR ($CDCl_3$) τ 2.42–3.00 (m, 10 H, arom), 5.35 (t, 1 H, J = 5 Hz, $-CH(-O-)-O-$), 6.08–6.30 (m, 4 H, $-O-(CH_2)_2-O-$), 6.95 (d, 1 H, J = 10 Hz, cyclopropyl benzylic), 7.20 (d, 1 H, J = 10 Hz, α-ketocyclopropyl), 7.19–7.38 (m, 1 H, α-ketocyclopentyl), 7.95 (d of d, 1 H, J_1 = 12, J_2 = 5 Hz, cyclopentyl), 8.10–9.30 (m, 7 H, aliph side chain and cyclopentyl); ir ($CHCl_3$) 3.41, 3.49, 3.84 (s), 6.24, 6.70, 6.91, 7.24, 7.79, 8.19, 8.79, 9.02, 9.29, 9.72, 10.23, 10.99, 14.38, and 15.14 μ.

Oxidation of *trans*-5,6-Diphenyl-*exo*-3-(4-iodobutyl)bicyclo-

[3.1.0]hexan-2-one. To a stirred suspension of 4.86 g of sodium bicarbonate in 70 ml of dimethyl sulfoxide[11] at 151° under nitrogen was added quickly 1.65 g (3.85 mmol) of *trans*-5,6-diphenyl-*exo*-3-(4-iodobutyl)bicyclo[3.1.0]hexan-2-one in 8 ml of dimethyl sulfoxide. After stirring for 4 min at 151°, the suspension was poured into ice–water and dichloromethane extracted. The combined organic extracts were dried and concentrated in vacuo to yield 1.71 g of a yellow oil which was chromatographed on three 25 cm × 25 cm × 2 mm silica gel plates (E. Merck AG Darmstadt, GF-254). After one development with chloroform, the plates were divided into five bands. The second band from the bottom contained 654 mg (2.06 mmol, 53%) of *trans*-5,6-diphenyl-*exo*-3-(4-oxobutyl)bicyclo[3.1.0]hexan-2-one as a colorless oil.

The spectral data were: ir ($CHCl_3$) 2.91, 3.26, 3.31, 3.38, 3.48, 3.52, 3.66, 5.83 (s), 6.23, 6.69, 6.91, 7.10, 7.20, 7.58, 8.23, 8.49, 8.68, 9.29, 9.71, 10.02, 10.62, 10.92, 11.03, 11.58, 12.16, 14.38, 15.13, and 15.88 μ; NMR ($CDCl_3$) τ 0.44 (t, 1 H, J = 1.5 Hz, -CHO), 2.69 (s, 10 H, arom), 6.53 (d, 1 H, J = 9 Hz, benzylic cyclopropyl), 7.24–7.52 (m, 1 H, -CO-CH), 7.34 (d, 1 H, J = 9 Hz, α-ketocyclopropyl), 7.54–8.14 (m, 3 H, -CH_2CHO and cyclopentyl), and 8.26–9.18 (m, 5 H, aliph side chain and cyclopentyl); MS *m/e* (%) 318 (12), 290 (1), 248 (8), 231 (4), 219 (12), 206 (100), 191 (18), 128 (25), 91 (75), 77 (14).

Ethylene Acetal of *trans*-5,6-Diphenyl-*exo*-3-(4-oxobutyl)bicyclo[3.1.0]hexan-2-one. A mixture of 282 mg (0.89 mmol) of *trans*-5,6-diphenyl-*exo*-3-(4-oxobutyl)bicyclo[3.1.0]hexan-2-one, 0.91 mmol (51 μl.) of ethylene glycol, and 3 mg of *p*-toluenesulfonic acid in 15 ml of benzene was refluxed for 7 hr under nitrogen with azeotropic removal of water. The solution was cooled, diluted with benzene, and washed with water, saturated sodium bicarbonate solution, and water again. The benzene layer was dried and concentrated in vacuo to give 315 mg of a yellow oil which was chromatographed on a 15 cm × 20 cm × 2 mm silica gel plate (E. Merck AG Darmstadt, GF-254). After one development with 50% ether in hexane, the plate was divided into five bands. The third band from the bottom contained 61 mg of the desired acetal as a colorless oil.

The spectral data were: NMR 2.52–2.95 (m, 10 H, arom), 5.24 (t, 1 H, J = 5 Hz, -CH(-O-)-O-), 6.04–6.25 (m, 4 H, -O-$(CH_2)_2$-O-), 6.88 (d, 1 H, J = 10 Hz, cyclopropyl benzylic), 7.28 (d, 1 H, J = 10 Hz, α-ketocyclopropyl), 7.30–7.50 (m, 1 H, α-ketocyclopentyl), 7.92 (d of d, 1 H, J_1 = 12, J_2 = 7 Hz, cyclopentyl), 8.20–9.20 (m, 7 H, aliph side chain and cyclopentyl); ir ($CHCl_3$) 3.36, 3.44, 5.85 (s), 6.24, 6.69, 6.91, 7.10, 7.22, 7.38, 7.57, 7.92, 8.11, 9.06, 9.71, 10.65, 11.02, 12.31, 14.38, and 15.49 μ.

Epimerization of the Ethylene Acetal of *trans*-5,6-Diphenyl-*endo*-3-(4-oxobutyl)bicyclo[3.1.0]hexan-2-one. A mixture of 110 mg (0.30 mmol) of the ethylene acetal of *trans*-5,6-diphenyl-*endo*-3-(4-oxobutyl)bicyclo[3.1.0]hexan-2-one and 2.0 g of sodium carbonate in 30 ml of dioxane and 10 ml of water was refluxed with stirring for 3 days and the dioxane removed in vacuo. The resultant milky solution was diluted with water and extracted with dichloromethane. The combined organic extracts were dried and concentrated in vacuo to give a yellow oil. The oil and 2.0 g of sodium carbonate were stirred and refluxed in 30 ml of tetrahydrofuran and 10 ml of water for 1 week, a procedure found to lead to product of improved purity. The tetrahydrofuran was removed in vacuo. Work-up as above yielded 106 mg of an oil whose NMR and ir were superimposable with those of the ethylene acetal of authentic *trans*-5,6-diphenyl-*exo*-3-(4-oxobutyl)bicyclo[3.1.0]hexan-2-one derived from the iodide oxidation and acetalization.

Photolysis of 1,2,6,7,8,8a-Hexahydro-2,2-diphenylnaphthalene. A solution of 559 mg (1.95 mmol) of 1,2,6,7,8,8a-hexahydro-2,2-diphenylnaphthalene in 500 ml of *tert*-butyl alcohol was purged with purified nitrogen[30] for 1 hr and then irradiated for 7 hr under purified nitrogen through a 2-mm Corex filter with a Hanovia 450-W medium-pressure mercury lamp in a quartz immersion well. The solvent was removed in vacuo to give a light-yellow oil which was chromatographed on a 2.5 × 135 cm column of a 3:1 mixture of silicic acid (Mallinkrodt Silic AR, CC-7, 200–325 mesh) and diatomaceous earth (Eagle Picher Celatom), slurry packed in hexane, monitoring by uv. Elution in 40-ml fractions gave: fractions 1–32, hexane, 22 mg; 33–38, 325 mg of mixture of *trans*-8,9-diphenyl-*exo*-tricyclo[4.4.0.$0^{8,10}$]dec-1-ene and *trans*-8,9-diphenyl-*endo*-tricyclo[4.4.0.$0^{8,10}$]dec-1-ene; 39–44, 61 mg of 1,2,6,7,8,8a-hexahydro-2,2-diphenylnaphthalene; 45–50, 54 mg of *cis*-8,9-diphenyl-*endo*-tricyclo[4.4.0.$0^{8,10}$]dec-1-ene; 51–60, 38 mg of *cis*-8,9-diphenyl-*exo*-tricyclo[4.4.0.$0^{8,10}$]dec-1-ene; and 61–70, 7 mg. The reactant as well as cis-endo and cis-exo products had identical ir and NMR spectra with those of the respective authentically synthesized compounds. The trans-exo and trans-endo product mixture was separated in the following experiment.

Separation of the *trans*-8,9-Diphenyltricyclo[4.4.0.$0^{8,10}$]dec-1-ene Isomers. High-pressure liquid chromatography was used for preparative separation of the two photoisomers. An ALC-100 liquid chromatograph (Waters Associates) was equipped with two 6 ft × ⅜ in. silicic acid columns (Mallinkrodt Silic AR, CC-7, 200–325 mesh), packed dry and eluted with hexane. In a typical injection of ca. 80 mg, the mixture was recycled up to seven times. By judicious trimming of the front and back of the peak, the slower moving *trans*-8,9-diphenyl-*endo*-tricyclo[4.4.0.$0^{8,10}$]dec-1-ene (19 mg) could be separated from the faster moving *trans*-8,9-diphenyl-*exo*-tricyclo[4.4.0.$0^{8,10}$]dec-1-ene (8 mg). Further recycling was needed for separation of the overlapped portions (50 mg).

The spectral data of *trans*-8,9-diphenyl-*endo*-tricyclo[4.4.-0.$0^{8,10}$]dec-1-ene were: NMR ($CDCl_3$) τ 2.50–2.88 (m, 10 H, arom), 4.32 (m, 1 H, vinyl), 6.88–7.42 (m, 1 H, tertiary allylic), 7.20 (d, 1 H, J = 10 Hz, benzylic cyclopropyl), 7.33 (d, 1 H, J = 10 Hz, allylic cyclopropyl), 7.70 (d of d, 1 H, J_1 = 13, J_2 = 3 Hz, cyclopentyl), 7.82–9.00 (m, 7 H, aliph); ir ($CHCl_3$) 3.25, 3.31, 3.40, 3.48, 5.13, 5.33, 5.55, 5.80, 5.97, 6.24, 6.69, 6.91, 7.51, 8.61, 8.71, 9.31, 9.73, 9.84, 10.31, 10.62, 10.87, 11.00, 11.73, 12.18, 14.41, 15.08, and 15.53 μ; uv λ_{max} (EtOH) 202 nm (ϵ 31,000), sh 217 (16,250), 255 (1900), 270 (90).

The trans-exo product had ir and NMR spectra identical with those of the independently synthesized material (vide supra).

Sensitized Photolysis of 1,2,6,7,8,8a-Hexahydro-2,2-diphenylnaphthalene. A solution of 376 mg (1.32 mmol) of 1,2,6,7,8,8a-hexahydro-2,2-diphenylnaphthalene and 50 mg of *m*-methoxyacetophenone (0.34 mmol) in 500 ml of *tert*-butyl alcohol was purged with purified nitrogen[30] for 1.5 hr and then irradiated for 18 hr through a 2-mm Pyrex filter with a Hanovia 450-W medium-pressure mercury lamp in a quartz immersion well. The solvent was removed in vacuo to yield a clear oil which was chromatographed on a 2 × 31 cm silica gel column (Grace, grade 62, 60–200 mesh), slurry packed in hexane. Elution in 125-ml fractions gave: fractions 1–6, hexane, 340 mg of starting diene plus tricyclic photoproducts; 7, hexane, nil; 8–10, 10% ether in hexane, 50 mg of *m*-methoxyacetophenone. Fractions 1–6 were chromatographed on a 2.5 × 139 cm column of a 3:1 mixture of silicic acid (Mallinkrodt Silic AR, CC-7, 200–325 mesh) and diatomaceous earth (Eagle-Picher Celatom), slurry packed in hexane. Elution in 40-ml fractions gave: fractions 1–27, hexane, 10 mg; 28–32, 31 mg of a mixture of *trans*-8,9-diphenyl-*exo*-tricyclo[4.4.0.$0^{8,10}$]dec-1-ene and *trans*-8,9-diphenyl-*endo*-tricyclo[4.4.0.$0^{8,10}$]dec-1-ene; 33–38, 210 mg of 1,2,6,7,8,8a-hexahydro-2,2-diphenylnaphthalene; 39–42, 61 mg of 1,2,6,7,8,8a-hexahydro-2,2-diphenylnaphthalene and *cis*-8,9-diphenyl-*endo*-tricyclo[4.4.0.$0^{8,10}$]dec-1-ene; and 43–54, 18 mg of a mixture of *cis*-8,9-diphenyl-*endo*-tricyclo[4.4.0.$0^{8,10}$]dec-1-ene and *cis*-8,9-diphenyl-*exo*-tricyclo[4.4.0.$0^{8,10}$]dec-1-ene.

Irradiation of 2,6,7,7a-Tetrahydro-6,6-diphenylindene in Pentane with Methanol Work-up. A solution of 0.150 g (0.550 mmol) of 2,6,7,7a-tetrahydro-6,6-diphenylindene in 125 ml of pentane was degassed with purified nitrogen[30] and irradiated for 30 min through a 2-mm Corex filter with a Hanovia 450-W medium-pressure mercury lamp in a quartz immersion well. Immediately after the light was turned off, 50 ml of anhydrous methanol was added. The mixed solvents were immediately removed in vacuo at room temperature, and a NMR spectrum was taken on the 155 mg of colorless oily residue. In addition to starting diene, signals were present for the *trans*-8,9-diphenyl-*endo*-tricyclo[6.1.0.$0^{2,6}$]non-2-ene. Vapor-phase chromatographic analysis on a 0.25 in. × 5 ft 3.5% diethylene glycol succinate (DEGS) on Varaport 30, 100–120 mesh column at 151°, showed that small amounts of the trans,exo, cis,endo, and cis,exo bicyclic olefins were also present. Infrared analysis of the crude residue showed a conspicuous lack of hydroxy or carbonyl peaks. No methoxy groups could be discerned in the NMR. The reaction spectra were identical with the spectra of the photolysis run in *tert*-butyl alcohol.

Irradiation of 2,6,7,7a-Tetrahydro-6,6-diphenylindene in Methanol. A solution of 0.120 g (0.440 mmol) of 2,6,7,7a-tetrahydro-6,6-diphenylindene in 125 ml of anhydrous methanol was degassed

with purified nitrogen[30] for 1 hr and irradiated for 1 hr through a 2-mm Corex filter with a Hanovia 450-W medium-pressure mercury lamp in a quartz well. The solvent was removed in vacuo at room temperature to yield 125 mg of a colorless oil. Vapor-phase analysis, infrared analysis, and NMR analysis gave no indication that any methanol adducts were formed, or that any bicyclobutane products were generated. This conclusion was derived from the observation that no hydroxy, methoxy, or carbonyl absorptions were noted. The absorption spectra as well as the VPC analysis were identical with those observed when the photolysis was run in *tert*-butyl alcohol or pentane.

Photolysis Equipment and Quantum Yield Determinations for 2,6,7,7a-Tetrahydro-6,6-diphenylindene. Direct quantum yields were performed on the black box apparatus.[12] Light output was monitored by ferrioxalate actinometry, and the light absorbed in the reaction cell was determined by the splitting ratio technique previously described.[12] The band pass was controlled by the following filter solution (Filter solution A): 2.0 *M* $NiSO_4 \cdot 6H_2O$ in 5% H_2SO, 1.0 *M* $CoSO_4 \cdot 7H_2O$ in 5% H_2SO_4, 2×10^{-4} *M* $BiCl_3$ in 10% HCl; transmission, 0% at 250 nm, 5% at 255 nm, 25% at 270 nm, 25% at 290 nm, 3% at 300 nm, 0% at 305 nm. The sensitized quantum yields were performed on an L-shaped optical bench previously described.[12] The light source was an Osram HBO 200-W super-pressure mercury lamp in series with a Bausch and Lomb high-intensity monochromator. A wavelength of 330 nm with slit setting of 4.8 for the entrance and 2.8 for the exit of the monochromator was employed. These slit settings gave a band pass of less than 20 nm at half-peak height. Ferrioxalate actinometry and the splitting ratio technique were employed to measure the light absorbed.

The quantum yields were determined by VPC analysis using a 0.25 in. × 5 ft 3.5% diethylene glycol succinate (DEGS) on Varaport 30, 100–120 mesh column at 151° and flow of 15 ml/min. Phenanthrene was used as an internal standard. Retention times were: phenanthrene, 17 min; *cis*-8,9-diphenyl-*endo*-tricyclo[6.1.0.-$0^{2,6}$]non-2-ene, 27.5 min; *trans*-8,9-diphenyl-*endo*-tricyclo[6.1-.$0.0^{2,6}$]non-2-ene, 30 min; *trans*-8,9-diphenyl-*exo*-tricyclo[6.1.-$0.0^{2,6}$]non-2-ene, 34 min; *cis*-8,9-diphenyl-*exo*-tricyclo[6.1.0.-$0^{2,6}$]non-2-ene, 38 min; 2,6,7,7a-tetrahydro-6,6-diphenylindene, 60 min. The flame ionization detector of the Varian Aerograph Model 2100 gas chromatograph was calibrated for relative response of the compounds in the photolysate and the standard.

Summary of the Quantum-Yield Results for the Direct Irradiation of 2,6,7,7a-Tetrahydro-6,6-diphenylindene. For each of the direct runs, filter solution A was used, and 750 ml of *tert*-butyl alcohol, distilled from calcium hydride, was used as solvent. The data are listed as follows: starting 2,6,7,7a-tetrahydro-6,6-diphenylindene (mmol), light absorbed, *trans*-8,9-diphenyl-*endo*-tricyclo-[6.1.0.$0^{2,6}$]non-2-ene (mmol), quantum yield; *trans*-8,9-diphenyl-*exo*-tricyclo[6.1.0.$0^{2,6}$]non-2-ene (mmol), quantum yield, *cis*-8,9-diphenyl-*endo*-tricyclo[6.1.0.$0^{2,6}$]non-2-ene (mmol), quantum yield; *cis*-8,9-diphenyl-*exo*-tricyclo[6.1.0.$0^{2,6}$]non-2-ene (mmol), quantum yield; and percent conversion.

Run I-1. Starting five-ring diene (2.10 mmol), 0.995 mEinstein, trans,endo (0.107 mmol), ϕ = 0.108; trans,exo (0.008 mmol), ϕ = 0.008; cis,endo (0.001 mmol), ϕ = 0.001; cis,exo (0.0002 mmol), ϕ = 0.002; conversion 5%.

Run I-2. Starting five-ring diene (2.16 mmol), 0.553 mEinstein, trans,endo (0.0571 mmol), ϕ = 0.103; trans,exo (0.0038 mmol), ϕ = 0.007; cis,endo (0.00057 mmol), ϕ = 0.001; cis,exo (0.00137 mmol), ϕ = 0.002; conversion 3%.

Run I-3. Starting five-ring diene (2.25 mmol), 1.270 mEinsteins, trans,endo (0.116 mmol), ϕ = 0.091; trans,exo (0.0095 mmol), ϕ = 0.008; cis,endo (0.0025 mmol), ϕ = 0.002; cis,exo (0.0056 mmol), ϕ = 0.004; conversion 6%.

Summary of the Quantum-Yield Results for the Sensitized Irradiation of 2,6,7,7a-Tetrahydro-6,6-diphenylindene. For each of the sensitized runs on the optical bench, the wavelength employed was 330 ± 20 nm. 40 ml of *tert*-butyl alcohol, distilled from calcium hydride, was used as a solvent. Careful degassing with oxygen free nitrogen preceded each run. *m*-Methoxyacetophenone was used as the sensitizer in all runs. The data are listed as follows: starting 2,6,7,7a-tetrahydro-6,6-diphenylindene (mmol), *m*-methoxyacetophenone (mmol), mEinsteins of light absorbed by the sensitizer; *trans*-8,9-diphenyl-*endo*-tricyclo[6.1.0.$0^{2,6}$]non-2-ene (mmol), quantum yield; *trans*-8,9-diphenyl-*exo*-tricyclo[6.1.0.$0^{2,6}$]non-2-ene (mmol), quantum yield; *cis*-8,9-diphenyl-*endo*-tricyclo[6.1.0.-$0^{2,6}$]non-2-ene (mmol), quantum yield; *cis*-8,9-diphenyl-*exo*-tricyclo[6.1.0.$0^{2,6}$]non-2-ene (mmol), quantum yield; and percent conversion.

Run II-1. Starting five-ring diene (0.115 mmol), *m*-methoxyacetophenone (0.474 mmol), 0.0281 mEinstein; trans,endo (0.00589 mmol), ϕ = 0.209; trans,exo (0.00163 mmol), ϕ = 0.058; cis,endo (0.00103 mmol), ϕ = 0.036; cis,exo (0.0075 mmol), ϕ = 0.063; conversion 9%.

Run II-2. Starting five-ring diene (0.218 mmol), *m*-methoxyacetophenone (0.410 mmol), 0.0313 mEinstein; trans,endo (0.00708 mmol), ϕ = 0.227; trans,exo (0.00185 mmol), ϕ = 0.059; cis-endo (0.00060 mmol), ϕ = 0.019; cis,exo (0.00151 mmol), ϕ = 0.048; conversion 6%.

Run II-3. Starting five-ring diene (0.216 mmol), *m*-methoxyacetophenone (0.415 mmol), 0.0244 mEinstein; trans,endo (0.0551 mmol), ϕ = 0.248; trans,exo (0.0148 mmol), ϕ = 0.061; cis,endo (0.00032 mmol), ϕ = 0.013; cis,exo (0.00087 mmol), ϕ = 0.036; conversion 4%.

Photolysis Equipment and Quantum-Yield Determinations for 1,2,6,7,8,8a-Hexahydro-2,2-diphenylnaphthalene. Quantum-yield irradiations were performed on the black box apparatus.[12] Light output was monitored by ferrioxalate actinometry, and the light absorbed in the reaction cell was determined by the splitting ratio technique previously described.[12] The bandpass was controlled by one of the following filter solutions: filter B, 1.0 *M* $NiSO_4 \cdot 6H_2O$ in 5% H_2SO_4, 2.0 *M* $CoSO_4 \cdot 7H_2O$ in 5% H_2SO_4, 2×10^{-4} *M* $BiCl_3$ in 10% HCl; transmission, 0% at 254 nm, 37% at 280 nm, 0% at 304 nm; filter C, 1.0 *M* $NiSO_4 \cdot 6H_2O$ in 5% H_2SO_4, 1.0 *M* $CoSO_4 \cdot 7H_2O$ in 5% H_2SO_4, 0.015 *M* $SnCl_2 \cdot 2H_2O$ in 10% HCl; transmission, 0% at 300 nm, 35% at 323 nm, 0% at 360 nm.

The quantum yields were determined by VPC analysis using a 0.25 in. × 5 ft 3% Carbowax 20M on Varaport-30 column at 180° and 22 ml/min flow rate. Phenanthrene was used as an internal standard. Retention times were: phenanthrene, 12 min; *trans*-8,9-diphenyl-*exo*-tricyclo[4.4.0.$0^{8,10}$]dec-1-ene, 35 min; *trans*-8,9-diphenyl-*endo*-tricyclo[4.4.0.$0^{8,10}$]dec-1-ene, 40 min; *cis*-8,9-diphenyl-*exo*-tricyclo[4.4.0.$0^{8,10}$]dec-1-ene, 44 min; *cis*-8,9-diphenyl-*endo*-tricyclo[4.4.0.$0^{8,10}$]dec-1-ene, 49 min; 1,2,6,7,8,8a-hexahydro-2,2-diphenylnaphthalene, 63 min. The flame ionization detector of the Varian Aerograph Model 2100 gas chromatograph was calibrated for the relative response of the compounds in the photolysate and the standard.

Summary of the Quantum-Yield Results for the Direct Irradiation of 1,2,6,7,8,8a-Hexahydro-2,2-diphenylnaphthalene. For each of the direct runs, filter B was used, and 750 ml of *tert*-butyl alcohol, distilled from calcium hydride, was used as solvent. The data are listed as follows: starting 1,2,6,7,8,8a-hexahydro-2,2-diphenylnapthalene (mmol), light absorbed, *trans*-8,9-diphenyl-*endo*-tricyclo[4.4.0.$0^{8,10}$]dec-1-ene (mmol), quantum yield; *trans*-8,9-diphenyl-*exo*-tricyclo[4.4.0.$0^{8,10}$]dec-1-ene (mmol), quantum yield; *cis*-8,9-diphenyl-*endo*-tricyclo[4.4.0.$0^{8,10}$]dec-1-ene (mmol), quantum yield; *cis*-8,9-diphenyl-*exo*-tricyclo[4.4.0.$0^{8,10}$]dec-1-ene (mmol), quantum yield; and percent conversion.

Run III-1. Starting six-ring diene (1.88 mmol), 0.619 mEinstein, trans,endo (0.057 mmol), ϕ = 0.093; trans,exo (0.018 mmol), ϕ = 0.029; cis,endo (0.00056 mmol), ϕ = 0.0009; cis,exo (0.00026 mmol), ϕ = 0.0004; conversion 4%.

Run III-2. Starting six-ring diene (1.71 mmol), 0.897 mEinstein, trans,endo (0.086 mmol), ϕ = 0.096; trans,exo (0.030 mmol), ϕ = 0.033; cis,endo (0.0013 mmol), ϕ = 0.0014; cis,exo (0.00054 mmol), ϕ = 0.0006; conversion 7%.

Run III-3. Starting six-ring diene (1.90 mmol), 1.34 mEinsteins, trans,endo (0.12 mmol), ϕ = 0.091; trans,exo (0.040 mmol), ϕ = 0.030; cis,endo (0.0012 mmol), ϕ = 0.0009; cis,exo (0.00044 mmol), ϕ = 0.0003; conversion 9%.

Summary of the Quantum-Yield Results for the Sensitized Irradiation of 1,2,6,7,8,8a-Hexahydro-2,2-diphenylnaphthalene. For each of the sensitized runs filter C was used and 750 ml of *tert*-butyl alcohol was used as solvent.

Run IV-1. Starting six-ring diene used (1.33 mmol), *m*-methoxyacetophenone (2.18 mmol), 19.94 mEinsteins; trans,endo (0.041 mmol), ϕ = 0.0021; trans,exo (0.0023 mmol), ϕ = 0.0010; cis,endo (0.00082 mmol), ϕ = 0.00004; cis,exo (0.00041 mmol), ϕ = 0.00002; conversion 4.8%.

Run IV-2. Starting six-ring diene (1.98 mmol), *m*-methoxyace-

tophenone (2.12 mmol), 17.65 mEinsteins; trans,endo (0.038 mmol), $\phi = 0.0021$; trans,exo (0.014 mmol), $\phi = 0.00078$; cis,endo (0.00072 mmol), $\phi = 0.00004$; cis,exo (0.00022 mmol), $\phi = 0.00001$; conversion 2.6%.

Emission Study of 2,6,7,7a-Tetrahydro-6,6-diphenylindene and 1,2,6,7,8,8a-Hexahydro-2,2-diphenylnaphthalene. Both bicyclic dienes **5** and **6** had fluorescence emissions at room temperature. The fluorescence lifetimes were measured by single-photon counting in conjunction with systematic reiterative convolution as previously described.[13a] An Aminco-Kiers spectrofluorimeter, equipped with an Hanovia 901C-1 xenon lamp, was used to obtain the fluorescence spectra. The emission work was done in mixed hydrocarbon solvent MCIP (methylcyclohexane–isopentane 4:1). Both hydrocarbon solvents were purified by repeated washing with 10% fuming sulfuric acid until the washings were colorless, then with water, then with 5% aqueous potassium hydroxide, and drying over phosphorus pentoxide. The solvent was then passed through a 3 × 70 cm alumina column containing 10% of silver nitrate.[31] The early and late fractions were discarded, and the solvents were transparent in the ultraviolet and fluorescence free.

Degassed solutions of bicyclic diene **5** fluoresced weakly at room temperature. Excitation was at 270 nm. The emission band extended from 310 to 390 nm with maximum emission at 340 (±5) nm. A blank run showed no fluorescence in this region. The measured lifetime was 1.97 nsec and, after shifting by no more than three channels, for optimum fit, the lifetime was 2.61 nsec (F value of 2.5).

Degassed solutions of bicyclic diene **6** fluoresced weakly at room temperature. Excitation at 280 nm led to an emission band that extended 310 to 390 nm with maximum emission at 340 (±5) nm. The measured lifetime was 1.71 nsec and, after shifting by no more than two channels, for optimum fit, the lifetime was 1.24 nsec (F value of 4.5).

The emission data for both of these bicyclic dienes and the *exo*-methylene diene (**1**) are summarized in Table III.

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References and Notes

(1) This is paper 94 of our photochemical series.
(2) For paper 93 of the series, note H. E. Zimmerman, K. S. Kamm, and D. P. Werthemann, *ibid.*, preceding paper in this issue.
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(14) (a) H. E. Zimmerman, D. P. Werthemann, and K. S. Kamm, *J. Am. Chem. Soc.*, **96**, 439 (1974). (b) The unpublished results of Kamm and Zimmerman indicate that degassed methylcyclohexane–isopentane solutions of *exo*-methylene diene (**1**) fluoresced very weakly at room temperature, but more strongly at 77 K. Using the method of magic multipliers,[14a] an average lifetime of 710 psec at room temperature was calculated. Kamm and Zimmerman report the following uv spectrum for **1**: sh 270, 263 nm (ϵ 220); λ_{max} 238 nm [ϵ 27,400 (lit.[3a] 31,600)]. They report that excitation at 240 nm gave an emission band from 260 to 320 nm with maximum emission at 270 (±5) nm.
(15) H. E. Zimmerman and R. D. Little, *J. Am. Chem. Soc.*, **94**, 8256 (1972).
(16) (a) Interestingly the oxa-di-π-methane rearrangement[5] seems also to be subject to changes in triplet decay as a function of the free rotor effect. Thus, Engel[16b] has noted molecular flexibility as one factor in decreasing oxa-di-π-methane reactivity. Indeed some evidence pointed to six-ring flexibility about a π bond affording lower reactivity than a comparable molecule with a five ring; however, other decay mechanisms (unspecified) were suggested as being more important. Also, Wagner[16c] has compared the triplet lifetimes of cyclopentenone and cyclohexenone, assuming similar rates of quenching, and has found excited cyclohexenone triplet to be shorter. Wagner noted this result to be in agreement with our free rotor effect. (b) P. S. Engel and M. A. Schexnayder, *J. Am. Chem. Soc.*, **94**, 9254 (1972); (c) P. J. Wagner and D. J. Bucheck, *ibid.*, **91**, 5090 (1969).
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(18) Although fluorescence quenching by dienes and alkenes is well known, we term our quenching mechanism touching. This cannot be quite the same as the ordinary process which is believed to go via an exciplex with face-to-face π systems since presently in our dienes both moieties are bonded to the methane carbon, and a parallel orientation is not likely (note ref 17a and 17d).
(19) The 0–0 singlet energy of an isolated phenyl S_1 is known[20] to be 105–108 kcal/mol. The precise 0–0 energy of an S_1 transoid diene is less well established. The 260–270 nm[21] maximum for isolated phenyl substituents compared with ca. 240 nm maximum for transoid dienes[22] suggests that the 0–0 singlet energy will also be lower for the phenyl chromophore. The 0–0 energy for S_1 of diphenylmethane and toluene are known to be 105 kcal/mol. However, the literature provides uncertain S_1 information, e.g., 100–125,[23] 90–92,[22] 90 kcal/mol[25] for butadiene. However, note ref 24 attributes the 90 kcal/mol value of ref 25 to absorption by cisoid butadiene conformers. In ref 22, the spectra were not well resolved, and the 0–0 transition band in the fluorescence emission was chosen as the "onset" of the curve, which could introduce large errors in the S_1 information.
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